

Supporting Information

Enzyme-like Supramolecular Iridium Catalysis Enabling C–H Bond Borylation of Pyridines with *meta*-Selectivity

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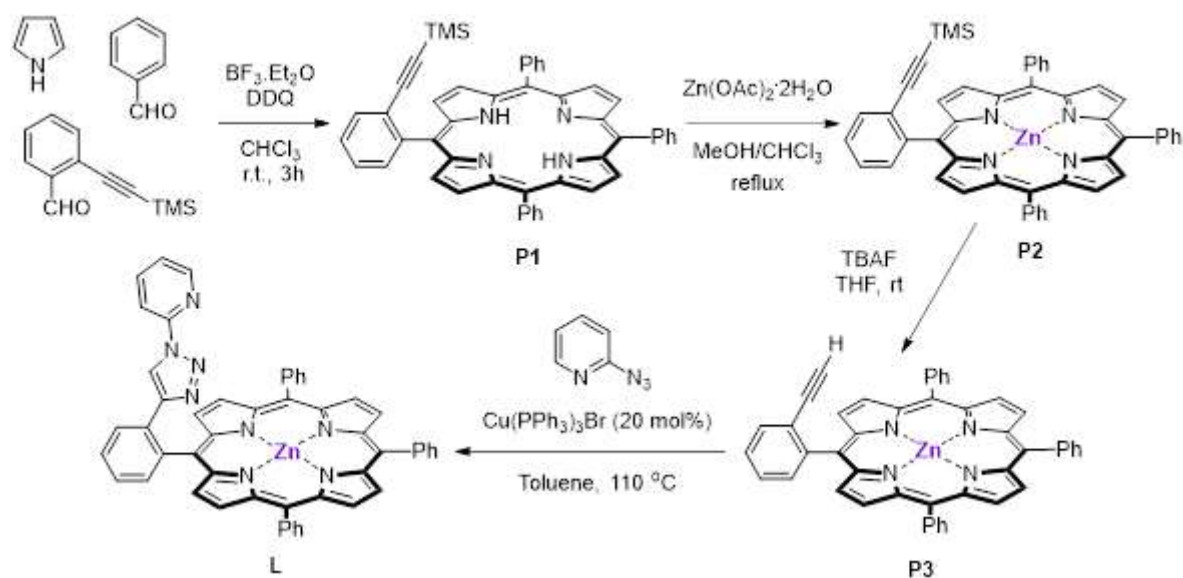
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1. General methods.

Solvents were purified with an MB SPS-800 purification system. Pyrrole was dried with CaH₂ and distilled prior to use. All solvent used for catalytic experiment were dried with CaH₂ and distilled prior to use. CDCl₃ was filtered through alumina and stored under argon over molecular sieves. All the other employed chemicals were purchased from commercial sources and used as received. Unless otherwise specified, reactions were carried out under argon atmosphere by employing standard Schlenk and vacuum-line techniques. ¹H and ¹³C NMR spectra were recorded with a Bruker GPX (400 MHz) spectrometer. ¹H NMR spectra were referenced to residual protiated solvent ($\delta = 7.26$ ppm for CDCl₃). ¹³C NMR spectra were referenced to CDCl₃ ($\delta = 77.16$ ppm). Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; hept, heptuplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublets of triplets. Coupling constants, *J*, were reported in hertz unit (Hz). The reactions were monitored by using a Shimadzu 2014 gas chromatograph equipped with an EquityTM-1 Fused Silica capillary column (30 m x 0.25 mm x 0.25 μ m) and an FID detector; conversion and selectivity were determined by using dodecane as internal standard. UV/Vis absorption spectra were recorded with a Specord 205 UV/Vis/NIR spectrophotometer and quartz cuvettes of 1 cm path length. Mass spectroscopy and microanalysis were performed in the laboratories of the Centre Regional de Mesures Physiques de l'Ouest (CRMPO, Université de Rennes 1, Rennes, France). Molecular modeling calculations were performed with the PM3-Spartan molecular modeling program.

2. Synthesis and characterization of the molecules employed in this study.

The supramolecular ligand **L** was synthesized according to the **Scheme S1** shown below:



Scheme S1. Synthetic pathway towards the supramolecular ligand **L**.

- **Synthesis and characterization of 2-((trimethylsilyl)ethynyl)benzaldehyde:** 2-Bromobenzaldehyde (1.57 mL, 2.49 mg, 13.5 mmol, 1 equiv.) was introduced into a dried Schlenk tube equipped with a stirring bar along with $\text{Pd}(\text{OAc})_2$ (0.037 mg, 0.14 mmol, 0.01 equiv.), CuI (0.0626 mg, 0.33 mmol, 0.025 equiv.) and PPh_3 (0.0909 mg, 0.29 mmol, 0.021 equiv.). Dry triethylamine (20 mL) was added to the reaction mixture and ethynyltrimethylsilane (2.2 mL, 1.56 mg, 16 mmol, 1,189 equiv.) was added slowly to the reaction mixture. The mixture was heated at 50°C over 18 hours after which GC-MS analysis showed full conversion of the starting materials. The crude mixture was filtered over celite with dichloromethane and the solvents evaporated under reduced pressure. The titled compound was further purified by column chromatography (SiO_2 , *n*-heptane:EtOAc 1:0 to 0:1) and isolated in 95% yield (2.6 g). ^1H NMR (400 MHz, CDCl_3): $\delta = 10.56$ (1H, s), 7.91 (1H, d, $J = 8.3$ Hz), 7.59-7.52 (2H, m), 7.44 (1H, t, $J = 7.8$ Hz), 0.28 (9H, s) ppm. The spectral data match those found in literature.^[1]

- **Synthesis and characterization of P1:** Distilled chloroform (650 mL), distilled pyrrole (1.4 mL, 20.2 mmol, 4 equiv.), benzaldehyde (1.53 mL, 15 mmol, 3 equiv.) and 2-((trimethylsilyl)ethynyl)benzaldehyde (1.01 g, 5.0 mmol, 1 equiv.) were introduced into a 1 L round bottom flask equipped with a stirring bar. At room temperature and under light protection, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (288 mg, 0.25 mL, 2.0 mmol, 0.4 equiv.) was added and the reaction was stirred for 3 hours. Then, DDQ (2.3 g, 10.0 mmol, 2 equiv.) was introduced and the reaction mixture was stirred for 1 hour before being quenched with Et_3N (0.282 μL). The solvent was evaporated and the crude mixture was purified by column chromatography (SiO_2 , *n*-heptane:DCM 9:1 to 6:4) affording **P1** as a purple powder (577 mg, 16% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.87$ -8.77 (8H, m, H_β), 8.23-8.13 (7H, m, $\text{H}_{\text{meso-aryl}}$), 7.9 (1H, dd, $J = 7.6, 1.5$ Hz, $\text{H}_{\text{meso-aryl}}$), 7.8-7.68 (11H, m, $\text{H}_{\text{meso-aryl}}$), -1.07 (9H, s), -2.73 (2H, s, $\text{H}_{\text{pyrrole}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR

(101 MHz, CDCl₃): δ = 144.88 (C _{α}), 142.32 (C _{α}), 134.84 (C_{meso-aryl}), 134.62 (C_{meso-aryl}), 134.52 (C_{meso-aryl}), 131.48 (C_{meso-aryl}), 128.06 (CH _{β}), 127.77 (CH _{β}), 127.75 (CH _{β}), 127.73 (CH _{β}), 127.30 (C_{meso-aryl}), 126.89 (C_{meso-aryl}), 126.74 (C_{meso-aryl}), 126.72 (C_{meso-aryl}), 120.42 (C_{meso-aryl}), 120.22 (C_{meso-aryl}), 120.04 (C_{meso-aryl}), 118.21 (C_{meso-aryl}), 105.15 (CH_{alkyne}), 99.46 (CH_{alkyne}), -1.23 (C_{TMS}) ppm. HRMS (ESI): m/z calcd for C₄₉H₃₉N₄Si 711.2938 [M+H]⁺; found: 711.2932 (1 ppm)

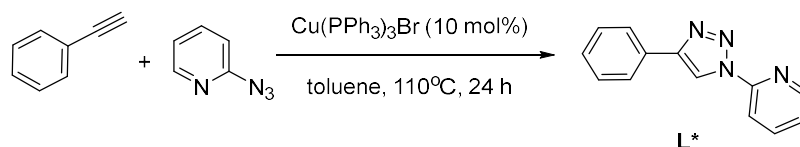
- **Synthesis and characterization of P2:** Porphyrin **P1** (607 mg, 0.853 mmol, 1 equiv.) was introduced into a 250 mL round bottom flask equipped with a stirring bar and MeOH:CHCl₃ (100 mL, v/v = 1:4). Zn(OAc)₂·2H₂O (0.603 mg, 2.75 mmol, 3.2 equiv.) was added and the reaction mixture was heated at reflux for 1 hour. Back at room temperature, the solvents were removed under reduced pressure and the crude mixture was purified over Alumina with DCM affording **P2** as a purple powder (660 mg, 99% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.95-8.86 (8H, m, H _{β}), 8.23-8.18 (7H, m, H_{meso-aryl}), 7.80-7.71 (11H, m, H_{meso-aryl}), 7.89 (1H, dd, J = 6.4, 2.7, H_{meso-aryl}), -1.14 (9H, s) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 150.69 (C _{α}), 150.38 (C _{α}), 150.36 (C _{α}), 150.07 (C _{α}), 145.67 (C_{meso-aryl}), 143.03 (C_{meso-aryl}), 143.01 (C_{meso-aryl}), 134.67 (C_{meso-aryl}), 134.55 (C_{meso-aryl}), 134.53 (C_{meso-aryl}), 134.50 (C_{meso-aryl}), 134.46 (C_{meso-aryl}), 132.30 (CH _{β}), 132.22 (CH _{β}), 132.18 (CH _{β}), 132.06 (CH _{β}), 132.03 (CH _{β}), 131.94 (CH _{β}), 131.42 (CH _{β}), 127.93 (CH_{meso-aryl}), 127.61 (CH_{meso-aryl}), 127.59 (CH_{meso-aryl}), 127.38 (CH_{meso-aryl}), 126.88 (CH_{meso-aryl}), 126.65 (CH_{meso-aryl}), 121.54 (C_{meso}), 121.16 (C_{meso}), 119.29 (C_{meso}), 105.52 (C_{alkyne}), 99.16 (C_{alkyne}), -1.11 (C_{TMS}) ppm. HRMS (ESI): m/z calcd for C₄₉ H₃₆ N₄ Si⁶⁴Zn 772.1995 [M]⁺; found: 772.1993 (0 ppm).

- **Synthesis and characterization of P3:** Porphyrin **P2** (500 mg, 0.56 mmol, 1 equiv.) was introduced in a dried Schlenk tube charged with a stirring bar and dry THF (20 mL). At room temperature, a solution of 1M TBAF in THF/water: 95/5 (0.56 mL, 1.94 mmol, 3 equiv.) was added dropwise and the mixture was stirred for 4 hours. Then, the mixture was evaporated to dryness and purified over neutral alumina using *n*-heptane:DCM (1:1) and afforded the analytically pure title porphyrin **P3** (431 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.95-8.82 (8H, m, H _{β}), 8.27-8.15 (7H, m, H_{meso-aryl}), 7.95 (1H, d, J = 8 Hz, H_{meso-aryl}), 7.76 (11H, m, H_{meso-aryl}), 2.12 (1H, s) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 150.29 (C _{α}), 150.21 (C _{α}), 150.18 (C _{α}), 150.05 (C _{α}), 145.50 (C_{meso-aryl}), 142.83 (C_{meso-aryl}), 142.78 (C_{meso-aryl}), 134.48 (CH_{meso-aryl}), 134.45 (CH_{meso-aryl}), 134.37 (CH_{meso-aryl}), 134.23 (CH_{meso-aryl}), 132.33 (CH _{β}), 131.99 (CH _{β}), 131.90 (CH _{β}), 131.47 (CH _{β}), 127.97 (CH_{meso-aryl}), 127.51 (CH_{meso-aryl}), 127.49 (CH_{meso-aryl}), 126.94 (CH_{meso-aryl}), 126.54 (CH_{meso-aryl}), 125.79 (C_{meso-aryl}), 121.44 (C_{meso}), 121.10 (C_{meso}), 118.63 (C_{meso}), 83.24 (C_{alkyne}), 80.95 (CH_{alkyne}) ppm. HRMS (ESI): m/z calcd for C₄₆ H₂₈ N₄⁶⁴Zn 700.1599 [M]⁺; found: 700.1600 (0 ppm).

- **Synthesis and characterization of 2-azidopyridine:** In a two-necked dried round bottom flask, 2-bromopyridine (1.23 mL, 2.06 mg, 13 mmol, 1 equiv.), sodium azide (1.6962 g, 26 mmol, 2 equiv.), CuI (0.2472 g, 1.3 mmol, 0.1 equiv.), sodium ascorbate (0.1472 g, 0.7 mmol, 0.05 equiv) and dimethylethyldiamine (0.21 mL, 0.172 mg, 1.95 mmol, 0.15 equiv.) were dissolved in a mixture of EtOH:H₂O (60 mL, v/v 7:3). Then, the reaction mixture was degassed by Argon followed by stirring during 2 hours at reflux. Back at room temperature, DCM:H₂O (200 mL, v/v 1:1) were added and the crude reaction mixture was transferred into a separatory funnel and 3 spoons of ethylene diamine tetraacetic acid disodium salt were added. The aqueous layer was extracted with DCM (3 x 20 mL) and the combined organic layers were washed water (2 x 50 mL). After drying over MgSO₄ and filtration, the solvents were

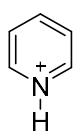
evaporated under reduced pressure. The product was further purified by filtration over Alumina using DCM as eluent affording 2-azidopyridine as a white powder (1.1 g, 70% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.84 (1H, d, J = 6.9 Hz, H_o), 8.07 (1H, d, J = 9 Hz, H_m), 7.71-7.66 (1H, ddd, J = 9.0, 6.8, 1.0 Hz, H_p), 7.25 (1H, dt, J = 9.0, 6.9 Hz, H_m) ppm. The spectral data match those found in literature.^[2]

- **Synthesis and characterization of L:** Into a dried Schlenk tube charged with a stirring bar, **P3** (220 mg, 0.31 mmol, 1 equiv.), 2-azidopyridine (0,070 mg, 0.58 mmol, 1.9 equiv.), $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (69 mg, 0.074 mmol, 0.2 equiv.) and dry toluene (15 mL) were added and the reaction mixture was stirred for 72 hours at 110 °C. Back at room temperature, the solvents were evaporated and the crude mixture was purified by column chromatography (SiO_2 , *n*-heptane:DCM, 1:1 to 0:1). The fraction containing the product were further purified by column chromatography (neutral Al_2O_3 , *n*-heptane:DCM, 1:1 to 0:1) affording **L1** as a purple powder (147 mg, 57% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.92-8.80 (8H, m, H_β), 8.74 (1H, d, J = 7.6 Hz, $\text{H}_{\text{meso-aryl}}$), 8.26-8.14 (7H, m, $\text{H}_{\text{meso-aryl}}$), 7.94 (1H, t, J = 8.3 Hz, $\text{H}_{\text{meso-aryl}}$), 7.77-7.67 (10H, m, $\text{H}_{\text{meso-aryl}}$), 7.59 (1H, d, J = 8.3 Hz, $\text{H}_{\text{meso-aryl}}$), 7.36 (1H, td, J = 8.1, 1.7 Hz, $\text{H}_{\text{meso-aryl}}$), 6.82 (1H, d, J = 5.0 Hz, $\text{H}_{\text{meso-aryl}}$), 6.58 (1H, m, $\text{H}_{\text{meso-aryl}}$), 5.41 (1H, s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 150.51 (C_α), 150.47 (C_α), 150.26 (C_α), 148.23 (C_{pyr}), 147.52 (CH_{pyr}), 147.43 (C_{triaz}), 142.95 ($\text{C}_{\text{meso-aryl}}$), 142.83 ($\text{C}_{\text{meso-aryl}}$), 140.43 ($\text{C}_{\text{meso-aryl}}$), 138.28 (CH_{pyr}), 135.38 ($\text{CH}_{\text{meso-aryl}}$), 134.65 ($\text{CH}_{\text{meso-aryl}}$), 134.58 ($\text{CH}_{\text{meso-aryl}}$), 134.52 ($\text{CH}_{\text{meso-aryl}}$), 132.85 (CH_β), 132.72 ($\text{C}_{\text{meso-aryl}}$), 132.16 (CH_β), 131.54 (CH_β), 128.80 ($\text{CH}_{\text{meso-aryl}}$), 127.91 ($\text{CH}_{\text{meso-aryl}}$), 127.69 ($\text{CH}_{\text{meso-aryl}}$), 127.66 ($\text{CH}_{\text{meso-aryl}}$), 126.83-125.99 (m, $\text{CH}_{\text{meso-aryl}}$), 122.60 (CH_{pyr}), 121.56 (C_{meso}), 121.37 (C_{meso}), 119.03 (C_{meso}), 118.66 (CH_{triaz}), 113.38 (CH_{pyr}) ppm. HRMS (ESI): m/z calcd for $\text{C}_{51}\text{H}_{32}\text{N}_8^{64}\text{Zn}$ 820.2036 $[\text{M}]^+$; found: 820.2035 (0 ppm).



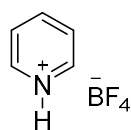
- **Synthesis and characterization of 2-(4-phenyl-1H-1,2,3-triazol-1-yl)pyridine (L*):** 2-azidopyridine (204.2 mg, 1.7 mmol, 1 equiv.) and $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (158.2 mg, 0.17 mmol, 0.1 equiv.) were suspended in dry toluene (12 mL) in a dry Schlenk tube. Then, ethynylbenzene (208.3 mg, 2 mmol, 1.18 equiv.) was introduced and the reaction mixture was stirred at 120 °C immediately for 24 hours. Back at room temperature, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (SiO_2 , *n*-heptane:EtOAc, 8:2 to 7:3) to afford **L*** (378 mg, 32% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.82 (1H, s, H_{triaz}), 8.54 (1H, d, J = 3.9 Hz, H_{pyr}), 8.26 (1H, d, J = 8.2 Hz, H_{pyr}), 7.94 (3H, m, H_{aryl}), 7.47 (2H, t, J = 7.5 Hz, H_{aryl}), 7.4-7.35 (2H, m, H_{pyr}) ppm. The spectral data match those found in literature.^[3]

- **Synthesis of pyridinium derivatives:**

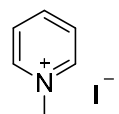


Pyridinium chloride: Dioxane (6 mL), pyridine (1 g, 1.02 mL, 1.3 mmol, 1 equiv.) and HCl (4 N in dioxane, 6.32 mL, 2.6 mmol, 2 equiv.) were added to an oven dried Schlenk flask. The reaction mixture was stirred overnight at room temperature. Then, the solvent was evaporated under reduced pressure yielding the pure

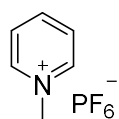
product as a solid (1.4 g, 96% yield). ^1H NMR (400 MHz, D_2O): δ = 8.73 (d, J = 5.8 Hz, 2H), 8.57 (t, J = 7.9 Hz, 1H), 8.02 (t, J = 7.0 Hz, 2H) ppm. The spectral data match those found in literature.^[4]



Pyridinium tetrafluoroborate: Dioxane (6 mL), pyridine (1 g, 1.02 mL, 1.3 mmol, 1 equiv.) and HBF_4^- (48% in diethyl ether, 2.28 mg, 4.6 mL, 2.6 mmol, 2 equiv.) were added to an oven dried Schlenk flask. The reaction mixture was stirred overnight at room temperature. Then, the solvent was evaporated under reduced pressure yielding the pure product as a solid (1.63 g, 75% yield). ^1H NMR (400 MHz, D_2O): δ = 9.02 (d, J = 6.0 Hz 2H), 8.79 (td, J = 7.5, 1.6 Hz, 1H), 8.25 (t, J = 7.5 Hz, 2H) ppm. ^{11}B $\{^1\text{H}\}$ NMR (128 MHz, D_2O): δ = -1.19 ppm. ^{19}F $\{^1\text{H}\}$ NMR (376 MHz, D_2O): δ = -151.46 ppm. The spectral data match those found in literature.^[5]



N-methylpyridinium iodide: THF (50 mL), pyridine (1 g, 1.02 mL, 13 mmol, 1 equiv.) and methyl iodide (2.15 g, 0.94 mL, 15 mmol, 1.2 equiv.) were added to an oven dried round bottom flask. The reaction mixture was stirred overnight at 70°C. Back at room temperature, the precipitate was filtered off and washed with cold THF yielding the pure product as a solid (1.5 g, 54% yield). ^1H NMR (400 MHz, D_2O): δ = 8.73 (d, J = 6.0 Hz, 2H), 8.47 (td, J = 7.1, 6.0 Hz, 1H), 7.99 (t, J = 7.1 Hz, 2H), 4.34 (s, 3H) ppm. The spectral data match those found in literature.^[6]



N-methylpyridinium hexafluorophosphate: Water (25 mL), *N*-methylpyridinium iodide (0.5 g, 2.3 mmol, 1 equiv.) and potassium hexafluorophosphate (0.417 g, 2.3 mmol, 1 equiv.) were added to an oven dried round bottom flask. The reaction mixture was stirred overnight at 100°C. Back at room temperature, the precipitate was filtered off and washed with cold water yielding the pure product as a solid (0.239 g, 47% yield). ^1H NMR (400 MHz, D_2O): δ = 8.72 (d, J = 6.1 Hz, 2H), 8.47 (t, J = 8.0 Hz, 1H), 7.99 (t, J = 6.4 Hz, 2H), 4.33 (d, J = 2.2 Hz, 3H) ppm. ^{19}F $\{^1\text{H}\}$ NMR (376 MHz, D_2O): δ = -72.13 (d, J = 706.5 Hz) ppm. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, D_2O): δ = 145.02 (hept, J = 706.5 Hz) ppm. The spectral data match those found in literature.^[7]

3. Coordination chemistry and substrate binding studies.

- **UV-vis titration between L and pyridine (binding experiment):** 20 mL solution (A) of L (2.4×10^{-4} M) in dry dichloromethane was prepared first. 8.3 mL of (A) were diluted to 100 mL using dry DCM to give the stock solution (B) of L (2×10^{-5} M, 100 mL) that will be employed as solvent to prepare solution (C) (for pyridine: 4×10^{-2} M, 5 mL). Next, solution (D) of pyridine (2.0×10^{-3} , 10 mL) was prepared by dilution of (B) using stock solution (A). Different aliquots of solution D were withdrawn and diluted with solution B to give a volume of 2 mL. UV-vis spectra of each sample were recorded by using 3 mL quartz cuvettes with 10 mm path length (Figure S1). The binding constant was evaluated by considering a 1:1 stoichiometry and using the software BindFit with Nelder-Mead method^[8] giving a value of $K_{1:1} = 5.7 \times 10^4 \pm 1.5 \text{ M}^{-1}$ (Figure S2).

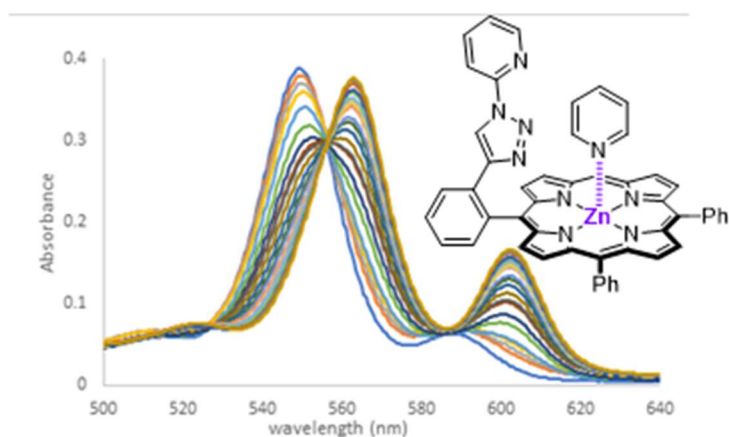


Figure S1. UV-vis spectra for L with pyridine to determine the binding constant.

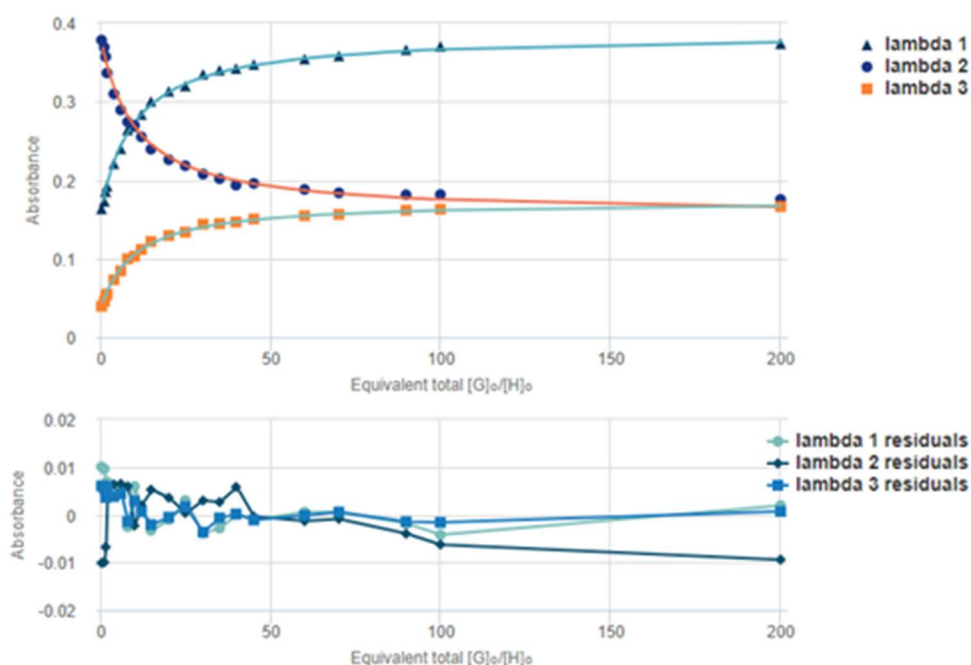


Figure S2. Curve fitting titration to determine the binding constant.

- **NMR binding experiment between L and pyridine (1:1 ratio):** L (3.25 mg, 3.95×10^{-3} mmol) was placed in an NMR tube and dried under vacuum for few minutes. Then, dry CDCl_3 (0.75 mL) was added and the corresponding ^1H NMR spectrum was recorded. A previously dried Schlenk tube was charged with dry pyridine (12.8 μL , 0.158 mmol) and CDCl_3 (1 mL): named stock solution A. Then, 1 equiv. of pyridine (25 μL of the stock solution A) were added to the NMR tube containing the ligand L and the corresponding ^1H NMR spectrum was recorded showing strong up-field shifts for the pyridine proton signals (Figure S3). ^1H NMR (400 MHz, CDCl_3): δ = 8.86-8.80 (8H, m, H_β), 8.59 (1H, d, $\text{H}_{\text{meso-aryl}}$), 8.20-8.15 (6H, m, $\text{H}_{\text{meso-aryl}}$), 8.04 (1H, d, J = 6.8 Hz, $\text{H}_{\text{meso-aryl}}$), 7.91 (1H, t, J = 7.1 Hz, $\text{H}_{\text{meso-aryl}}$), 7.75-7.56 (10H, m, $\text{H}_{\text{meso-aryl}}$), 7.44 (1H, d, J = 8.2 Hz, $\text{H}_{\text{meso-aryl}}$), 7.32 (1H, t, 8.2 Hz, $\text{H}_{\text{meso-aryl}}$), 7.21 (1H, d, J = 6.0 Hz, $\text{H}_{\text{meso-aryl}}$), 6.65-6.62 (1H, m, $\text{H}_{\text{meso-aryl}}$), 6.51 (1H, bs, $\text{H}_{p\text{-pyr}}$), 6.16 (1H, s, H_{triaz}), 5.86 (2H, bs, $\text{H}_{m\text{-pyr}}$), 4.16 (2H, bs, $\text{H}_{o\text{-pyr}}$) ppm.

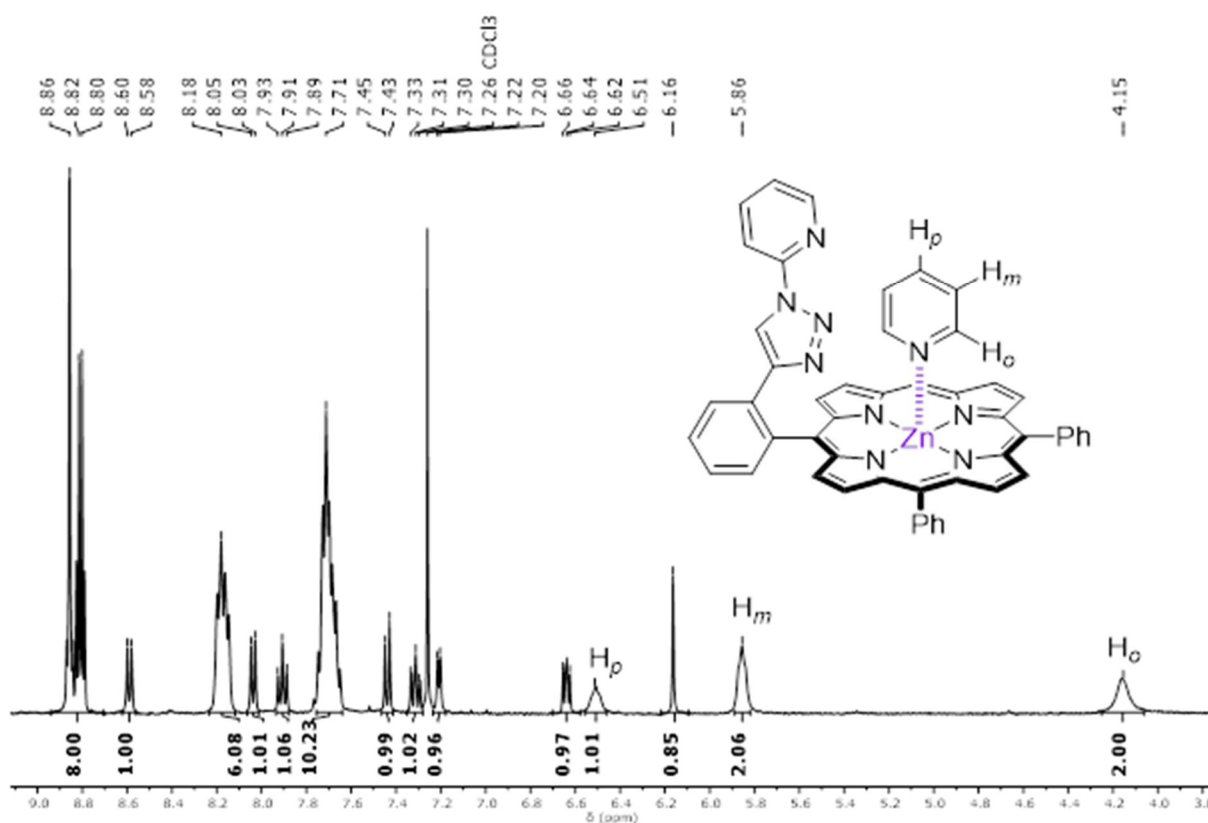


Figure S3. ^1H NMR spectrum (CDCl_3) of the self-assembly $[\text{L}:\text{pyridine}]$ in an equimolar ratio.

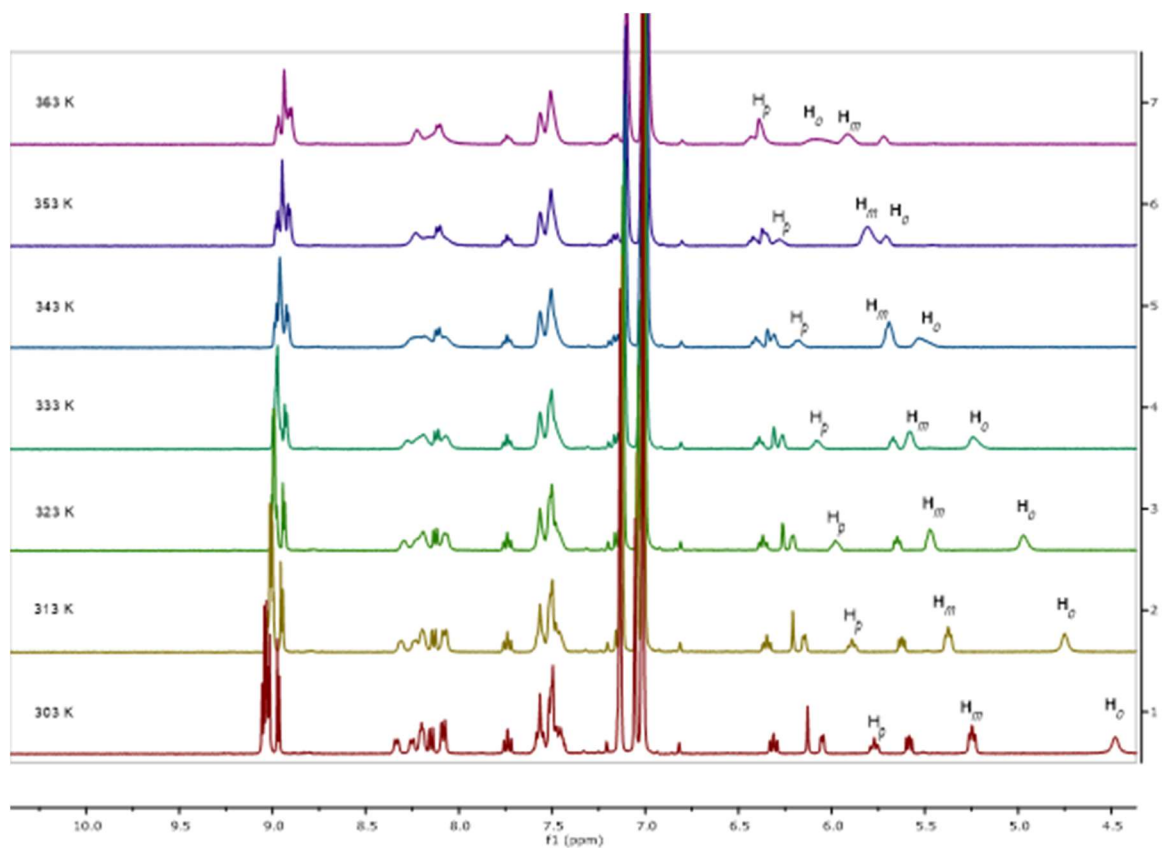


Figure S4. Variable high-temperature ¹H NMR (toluene-*d*⁸) spectra of pyridine and **L** in an equimolar ratio. It shows that the binding of pyridine to **L** is in fast exchange at the NMR time scale and it is kinetically labile in the range 25-90 °C (bottom to top).

- DOSY experiments:



Figure S5. DOSY experiment of pyridine and L in equimolar ratio (toluene-*d*⁸).

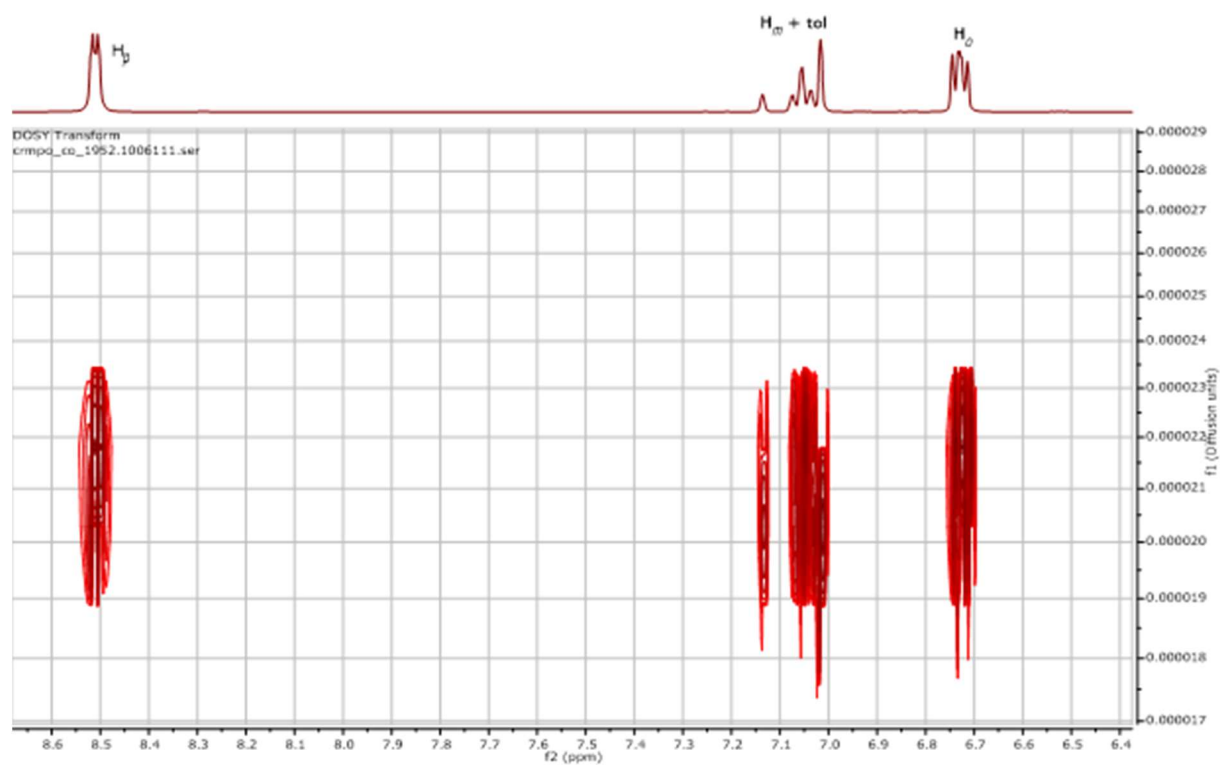


Figure S6. DOSY experiment of pure pyridine (toluene-*d*⁸).

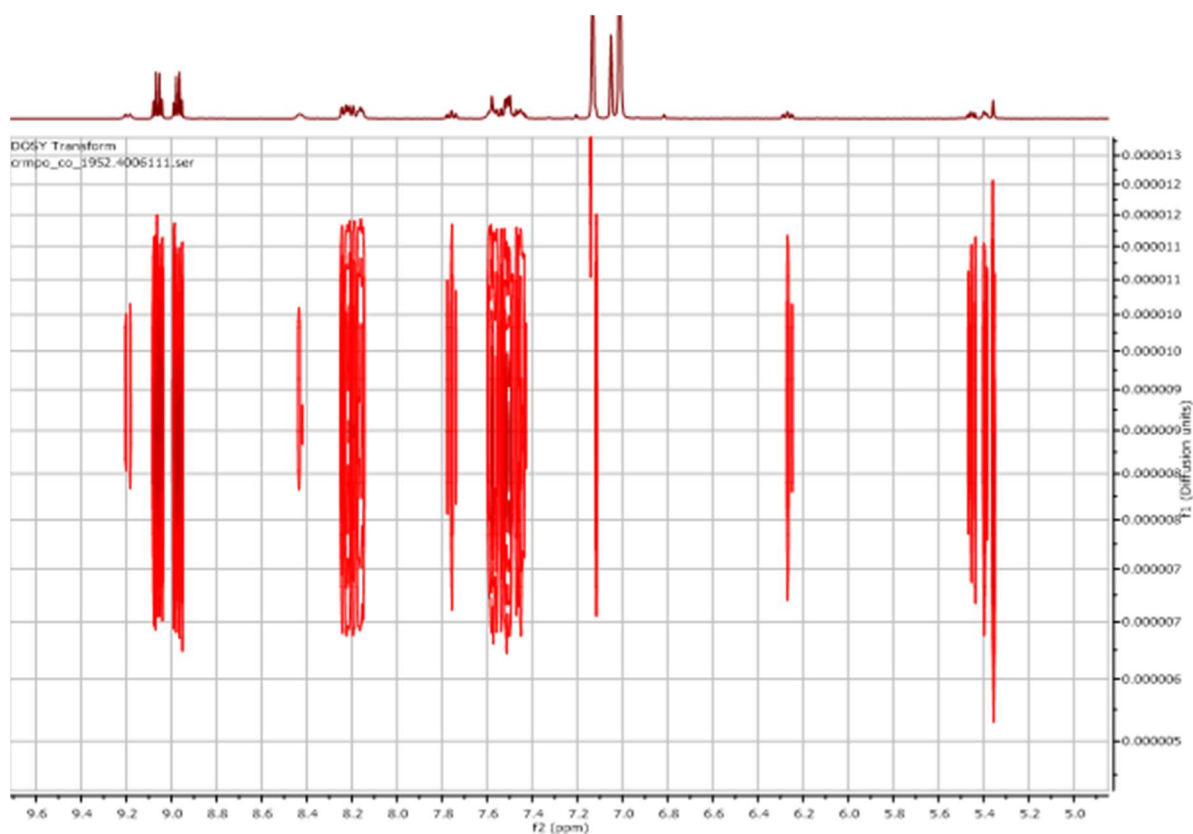


Figure S7. DOSY experiment of pure **L** (toluene- d^8).

The above-presented experiments indicate that the pyridine diffuses together with the supramolecular ligand **L** when both are together in solution. Qualitatively, the log D for the self-assembly [**L**:pyridine] is different than the ones derived from the individual partners.

- Coordination chemistry studies for the iridium complex L1: Into a dry Schlenk tube equipped with a stirring bar, **L** (4 mg, 4.86×10^{-3} mmol) and $[\text{Ir}(\text{COD})(\mu\text{-Cl})_2]$ (1.7 mg, 2.43×10^{-3} mmol) were introduced. After drying the reagents under vacuum for 30 minutes, dry DCM (1 mL) was added and the reaction mixture was stirred for 30 minutes at 60 °C. Back at room temperature, the solvents were removed under reduced pressure and the product was dried and characterized by NMR and HRMS. ^1H NMR (400 MHz, CDCl_3): δ = 8.95-8.84 (8H, m, H_β), 8.63 (1H, d, $J = 7.8$ Hz, $\text{H}_{\text{meso-aryl}}$), 8.23-8.14 (7H, m, $\text{H}_{\text{meso-aryl}}$), 7.95 (1H, t, $J = 7.8$ Hz, $\text{H}_{\text{meso-aryl}}$), 7.79-7.72 (10H, m, $\text{H}_{\text{meso-aryl}}$), 7.52 (1H, d, $J = 8.3$ Hz, $\text{H}_{\text{meso-aryl}}$), 7.34 (1H, d, $J = 7.9$ Hz, $\text{H}_{\text{meso-aryl}}$), 7.02 (1H, d, $J = 4.9$ Hz, $\text{H}_{\text{meso-aryl}}$), 6.60 (1H, t, $J = 6.2$ Hz, $\text{H}_{\text{meso-aryl}}$), 5.77 (1H, s, H_{triaz}), the proton singals from the COD ligand could not be detected due to broadness. HRMS (ESI): m/z calcd for $\text{C}_{59}\text{H}_{44}\text{N}_8^{64}\text{Zn}^{193}\text{Ir}$ 1121.2604 $[\text{M}]^+$; found: 1121.2599 (0 ppm). Note: Although minor changes were observed between the NMR signals of **L** and **L1** (Figure S8), the HRMS spectrum displayed a single peak unambiguously corresponding to the $[\text{Ir}(\text{COD})]$ fragment coordinated to the supramolecular ligand **L** resulting in a cationic species (Figure S9). A low temperature NMR experiment also supported the formation of a single species (Figure S10).

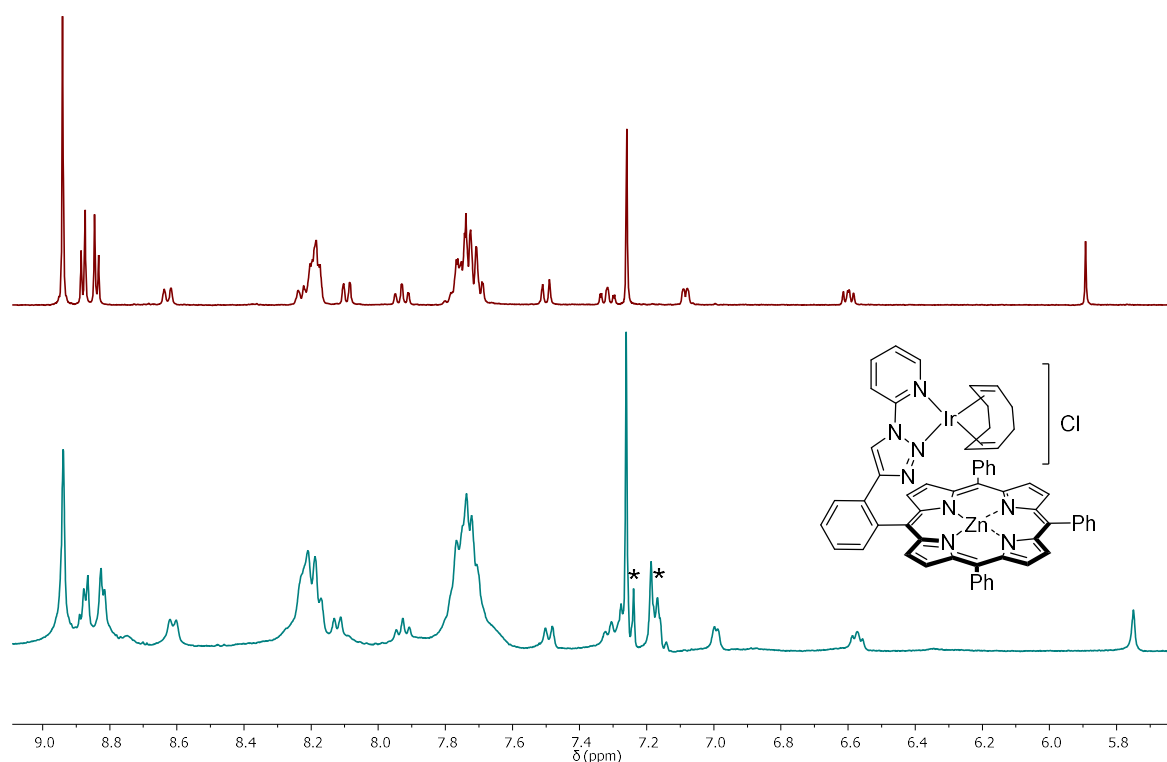


Figure S8. ^1H NMR (CDCl_3) spectra of **L** (top) and the iridium complex **L1** (bottom). *denotes traces of residual toluene solvent.

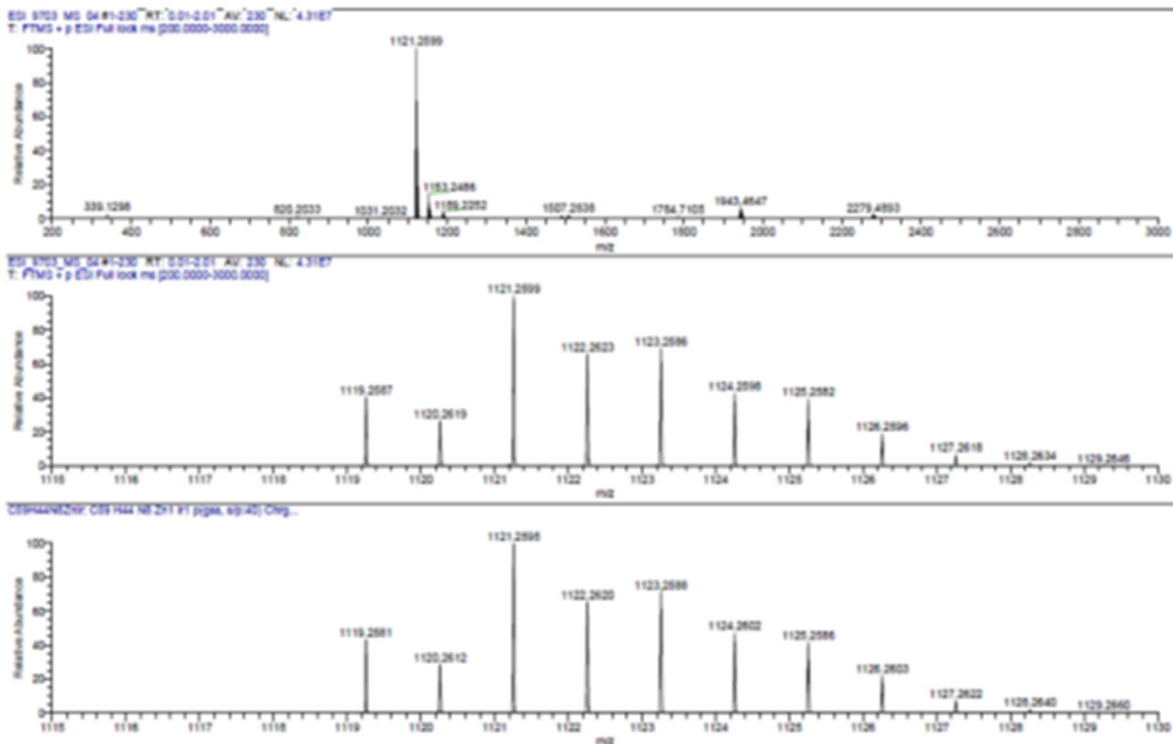


Figure S9. HRMS spectrum of the cationic iridium complex L1.

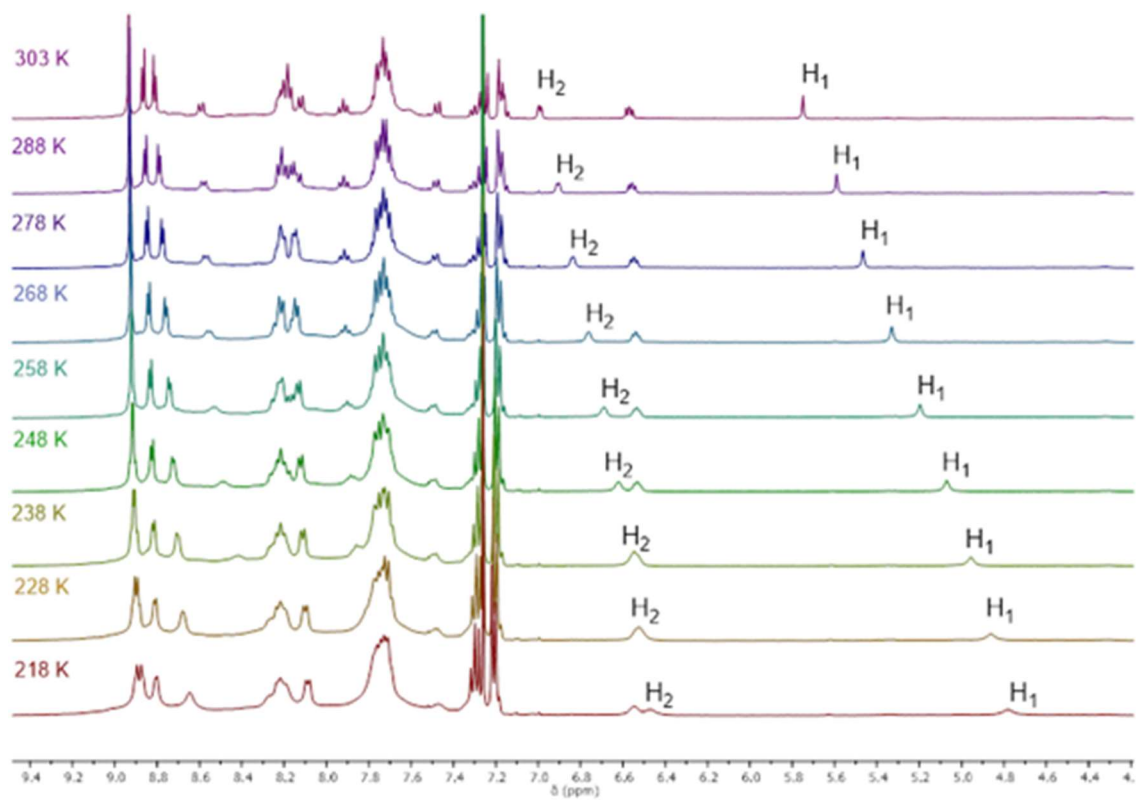


Figure S10. Variable low-temperature ^1H NMR (CDCl_3) spectra of the cationic iridium complex L1.

- **Competition experiments between L, pyridine and [Ir(COD)(μ -Cl)]₂ precursor:** Into a dry Schlenk tube equipped with a stirring bar, L (4 mg, 4.86×10^{-3} mmol) and [Ir(COD)(μ -Cl)]₂ (1.7 mg, 2.43×10^{-3} mmol) were introduced. After drying the reagents under vacuum for 30 minutes, dry DCM (1 mL) was added and the reaction mixture was stirred for 30 minutes at 60 °C. Back at room temperature, the solvents were removed under reduced pressure and the product was dried and analyzed by ¹H NMR confirming formation of the cationic iridium **L1** complex. Next, aliquots of pyridine in CDCl₃ (1 equiv., 2 equiv., and 3 equiv.) were subsequently added to the NMR tube and analyzed by ¹H NMR spectroscopy studies (Figure S11). In the presence of excess pyridine under the highly concentrated conditions required for NMR studies, pyridine preferentially binds to the zinc cation than to the iridium unit, as the proton signals from pyridine remain up-field shifted and they are not participating in any other equilibria than the one involving the zinc cation from the porphyrin L. This supports that pyridine binding to the zinc-porphyrin pocket is compatible with the iridium coordinating to the triazolopyridine chelating arm in the ligand L. This observation is corroborated in the case of the catalysis since they are performed in a more diluted media than in the experiments performed in the ¹H NMR studies. It seems plausible to evoke a top-bottom equilibria in which the coordination of pyridine occurs from a given side of the porphyrin plane at each time. If this likely occurs, this equilibria is fast at the NMR time scale because only one set of pyridine signals are observed even in the presence of an excess of pyridine (Scheme S2). No NOE cross-peaks were observed between the COD moiety and the pyridine. This was ascribed to the broadness of the COD proton signals and, also, to the fast equilibria shown in Scheme S2.

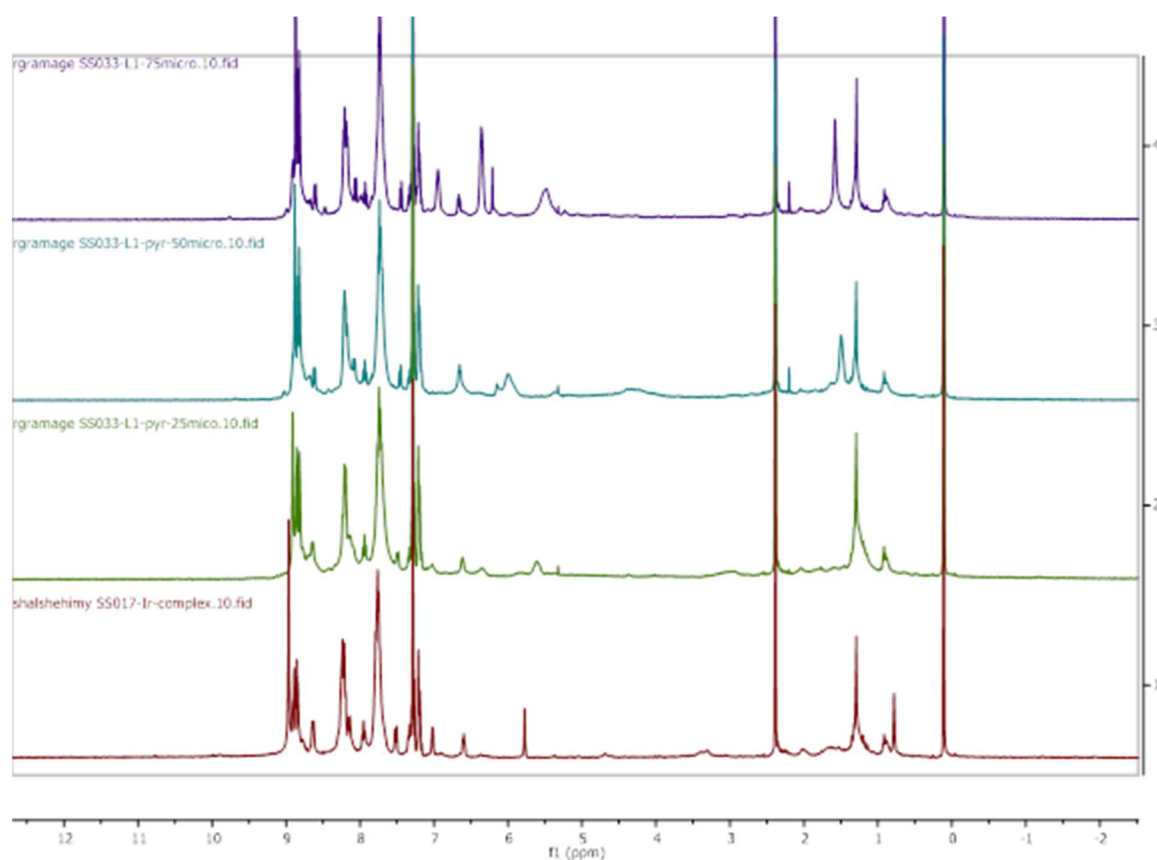


Figure S11. ¹H NMR (CDCl₃) spectra of the cationic iridium complex **L1** in the presence of increasing amounts of pyridine (0 to 3 equiv., bottom to top).

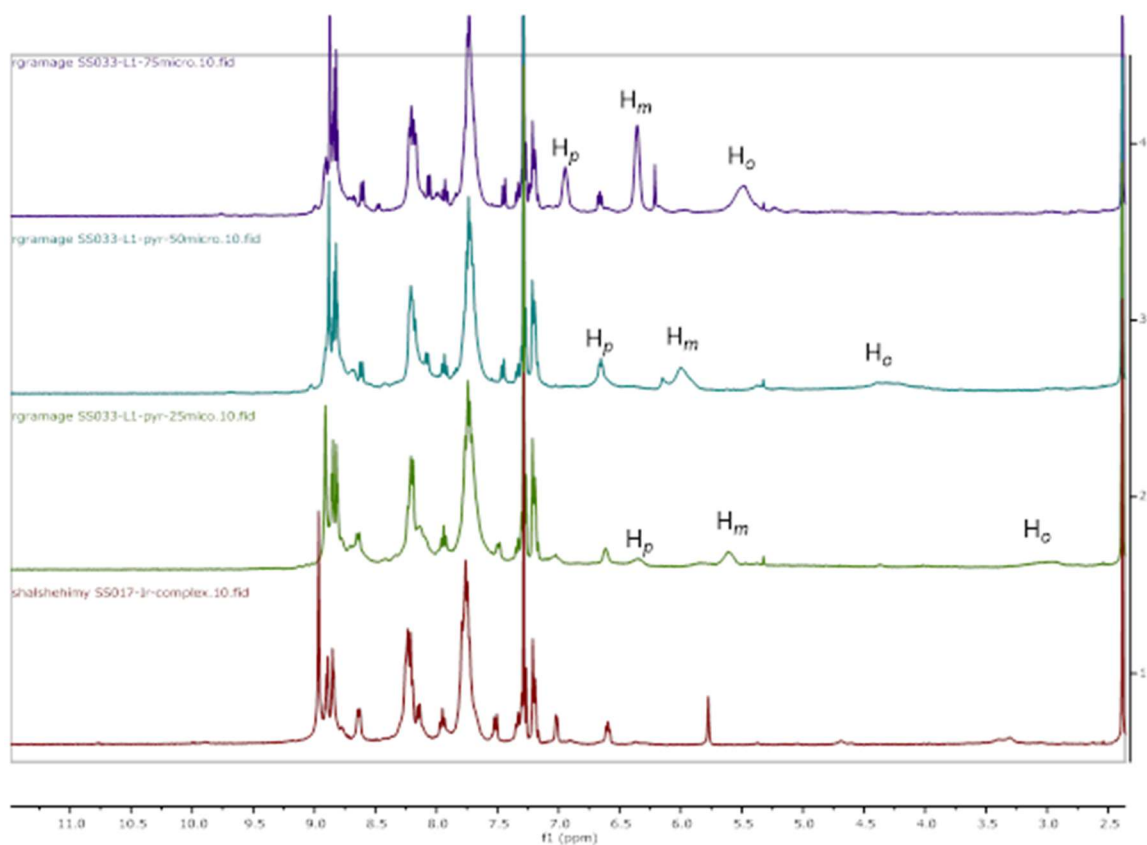
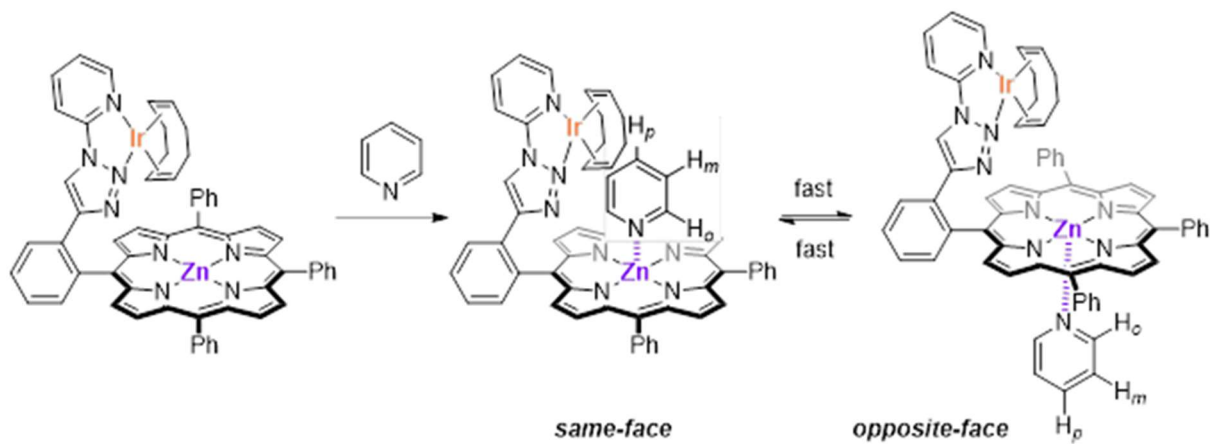


Figure S12. Zoom of the ^1H NMR (CDCl_3) spectra of the cationic iridium complex **L1** in the presence of increasing amounts of pyridine (0 to 3 equiv., bottom to top).



Scheme S2. Binding of pyridine to cationic iridium complex **L1** and postulated, fast top-bottom side equilibria.

- **NMR binding experiment between L and *N*-methylimidazole (1:1 ratio):** L (3.25 mg, 3.95×10^{-3} mmol) was placed in an NMR tube and dried under vacuum for few minutes. Then, dry CDCl_3 (0.75 mL) was added and the corresponding ^1H NMR spectrum was recorded. A previously dried Schlenk tube was charged with dry *N*-methylimidazole (10.4 μL , 130 μmol) and CDCl_3 (1 mL): named stock solution A. Then, 1 equiv of *N*-methylimidazole (30 μL of the stock solution A) were added to the NMR tube containing the ligand L and the corresponding ^1H NMR spectrum was recorded showing strong up-field shifts for the *N*-methylimidazole proton signals in accordance to $\text{Zn}^{\text{II}}\cdots\text{N}$ coordination (see below).

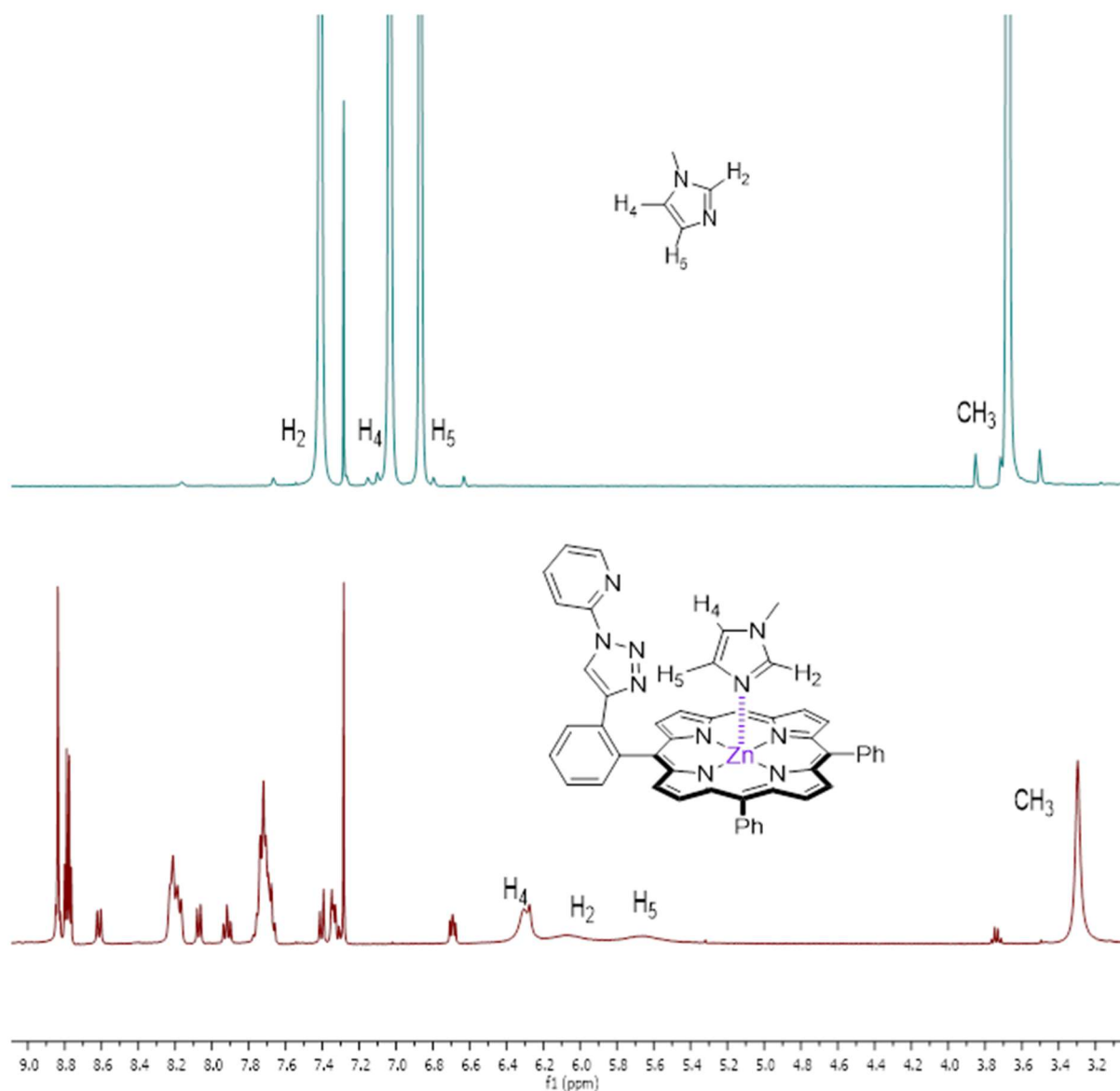


Figure S13. ^1H NMR (CDCl_3) spectra of *N*-methylimidazole (top) and of the assembly between *N*-methylimidazole and L (bottom) showcasing the up-field shifted protons from the substrate, thus indicating $\text{Zn}^{\text{II}}\cdots\text{N}$ coordination in solution.

4. XYZ cartesian coordinates for the modelled structures (PM3 calculations-Spartan).

The postulated species responsible for the regio-selectivity observed, namely the Ir(Bpin)₃(L)(pyridine) complex, was modelled with Spartan at the PM3-level of semi-empirical calculations (Figure S14). It shows that *meta*-C-H bond functionalization in the pyridine substrate is feasible. On the other hand, the protons in *ortho* and *para* from the pyridine are too far away from the iridium active site to be activated.

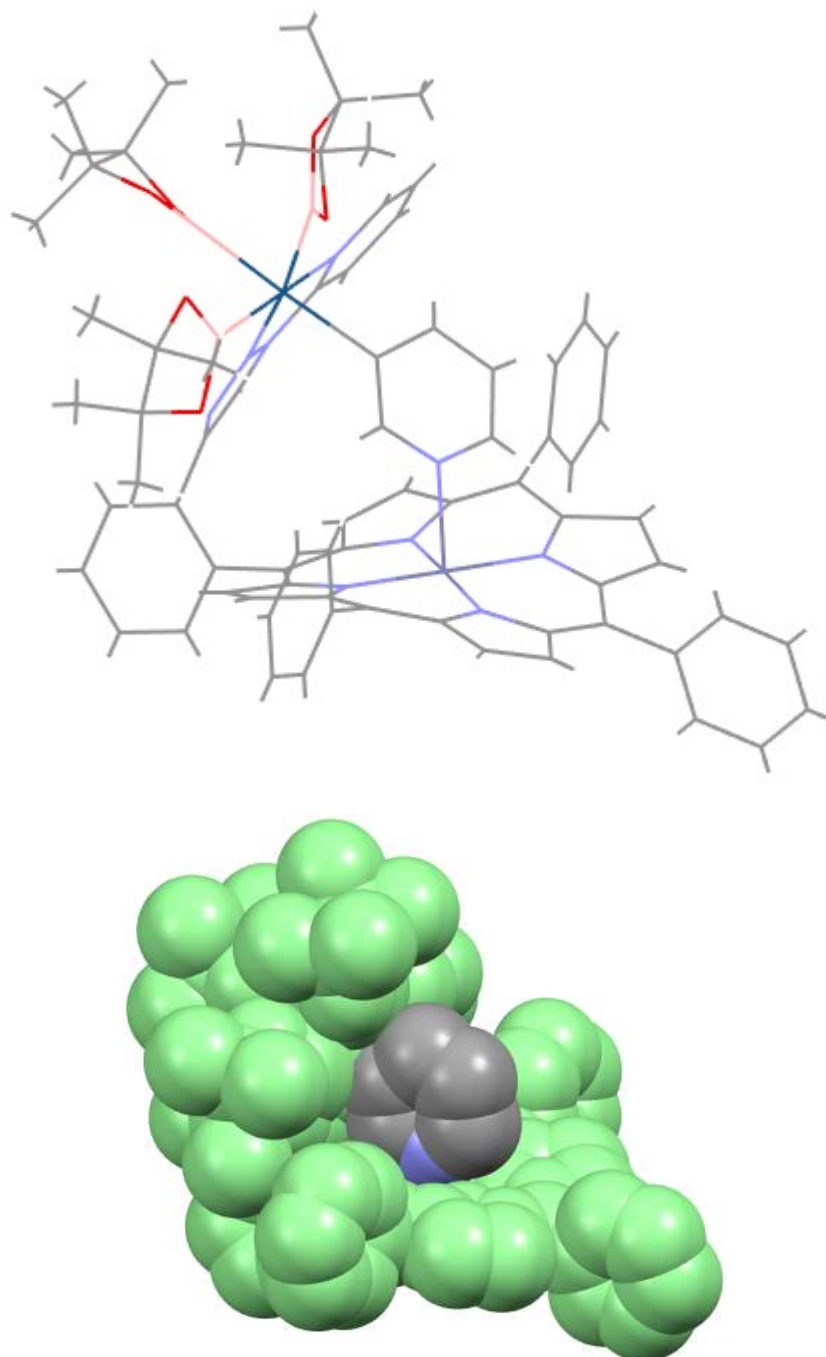


Figure S14. Molecular modelling (semi-empirical calculations) of the targeted supramolecular approach for pyridine functionalization. Top: wireframe representation, gray = carbon, blue = nitrogen, pink = boron, red = oxygen, green = iridium, dark blue = zinc. Bottom: van der Waals representation (hydrogen atoms omitted), green = catalyst, blue/gray = pyridine substrate.

N	2.676	-0.380	-0.951	C	-3.198	4.308	3.480	H	3.703	6.798	6.532
C	2.854	-0.375	-2.311	C	-1.042	6.026	3.112	H	4.893	8.097	6.291
C	3.849	-0.632	-0.291	C	-3.390	5.541	2.857	H	5.285	6.418	5.883
C	4.195	-0.661	-2.524	N	-0.886	4.841	3.711	H	5.410	8.888	3.809
C	.819	-0.785	-1.271	Ir	1.010	4.159	4.429	H	5.981	7.215	3.646
C	3.977	-0.763	1.118	C	2.167	4.054	0.148	H	4.834	7.838	2.489
C	2.929	-0.942	1.943	C	1.217	2.264	1.893	H	3.438	10.099	5.204
N	1.618	-0.828	1.670	C	1.817	2.751	-0.190	H	2.626	9.048	6.394
C	0.921	-1.202	2.738	C	2.001	4.473	1.453	H	1.669	9.954	5.252
C	1.821	-1.575	3.841	C	1.511	3.546	2.352	H	3.042	9.524	2.632
C	3.031	-1.363	3.326	N	1.360	1.928	0.667	H	2.344	7.939	2.225
C	-0.526	-1.170	2.946	Zn	0.844	-0.118	-0.018	H	1.327	9.178	2.928
C	-1.254	-0.558	2.002	B	2.749	3.218	5.323	H	-2.137	2.155	-3.655
N	-0.889	0.038	0.801	B	0.454	4.826	6.421	H	-0.146	1.095	-4.956
C	-1.937	0.801	0.301	B	2.145	6.023	4.320	H	3.131	1.772	-4.848
C	-2.675	-0.257	2.175	O	1.616	7.299	4.703	H	3.652	1.567	-7.260
C	-3.049	0.613	1.232	O	3.537	6.083	3.964	H	2.999	-0.475	-8.506
C	-2.056	1.517	-0.823	C	3.967	7.379	4.439	H	1.825	-2.323	-7.339
C	-1.037	1.278	-1.837	C	4.490	7.171	5.868	H	1.297	-2.135	-4.929
N	0.110	0.617	-1.720	C	5.107	7.869	3.549	H	4.683	-0.737	-3.489
C	0.653	0.470	-2.940	C	2.666	8.239	4.368	H	5.867	-0.999	-1.098
C	-1.296	1.630	-3.242	C	2.609	9.400	5.357	H	5.525	-2.982	1.572
C	-0.275	1.065	-3.886	C	2.338	8.752	2.958	H	7.810	-3.041	2.524
C	1.849	-0.056	-3.266	O	1.401	5.318	7.375	H	8.942	-0.934	3.179
C	2.105	-1.426	-6.792	O	-0.890	4.840	6.915	H	7.787	1.243	2.882
C	2.837	0.875	-5.388	C	0.658	5.395	8.611	H	5.494	1.316	1.945
C	1.808	-1.317	-5.433	C	-0.809	5.620	8.131	H	3.953	-1.531	3.857
C	2.766	-0.387	-7.448	C	-1.884	5.131	9.098	H	1.568	-1.901	4.832
C	3.133	0.762	-6.747	C	-1.111	7.069	7.719	H	-2.151	-0.469	7.314
C	2.168	-0.164	-4.722	C	1.236	6.528	9.455	H	-2.561	-2.886	7.624
C	-4.280	4.544	-1.111	C	0.874	4.058	9.331	H	-2.055	-4.485	5.799
C	-4.409	1.804	-1.642	H	-2.262	4.171	-0.458	H	-1.125	-3.681	3.657
C	-5.447	3.987	-1.634	H	-4.227	5.613	-0.924	H	-3.309	-0.636	2.960
C	-3.176	3.730	-0.849	H	-6.305	4.621	-1.848	H	-4.041	1.022	1.126
C	-3.236	2.355	-1.111	H	-6.419	2.189	-2.318	O	3.706	3.921	6.118
C	-5.512	2.620	-1.900	H	-4.466	0.740	-1.864	O	3.039	1.791	5.236
C	-1.104	-1.596	4.248	H	-4.032	3.626	3.612	C	4.752	2.955	6.353
C	-2.157	-2.522	6.681	H	-4.382	5.825	2.508	C	4.004	1.589	6.295
C	-1.349	-2.964	4.445	H	-2.451	7.366	2.179	C	5.774	3.144	5.222
C	-1.398	-0.685	5.293	H	-0.162	6.641	2.991	C	5.408	3.268	7.695
C	-1.924	-1.158	6.503	H	-0.369	7.445	7.006	C	4.896	0.397	5.967
C	-1.873	-3.422	5.655	H	-1.137	7.741	8.583	C	3.188	1.271	7.557
C	5.995	0.359	2.077	H	-2.079	7.132	7.209	H	4.667	3.338	8.499
C	7.298	-2.089	2.403	H	-2.884	5.316	8.691	H	5.902	4.246	7.665
C	5.346	-0.829	1.710	H	-1.809	5.633	10.068	H	6.154	2.514	7.965
C	7.286	0.320	2.605	H	-1.826	4.048	9.252	H	6.133	4.179	5.193
C	7.935	-0.904	2.771	H	0.391	4.042	10.313	H	5.324	2.953	4.241
C	6.009	-2.054	1.869	H	1.943	3.866	9.475	H	6.641	2.487	5.343
C	-1.206	0.741	5.124	H	0.490	3.219	8.739	H	5.306	0.470	4.957
C	-2.244	1.633	4.795	H	2.268	6.304	9.748	H	4.322	-0.536	5.994
H	-3.308	1.505	4.669	H	1.288	7.466	8.892	H	5.721	0.304	6.679
N	0.056	1.363	5.142	H	0.649	6.690	10.365	H	3.831	1.050	8.414
N	-0.233	2.571	4.752	H	0.847	1.510	2.573	H	2.525	2.100	7.821
N	-1.552	2.770	4.488	H	1.931	2.410	-1.214	H	2.536	0.406	7.387
C	-1.916	3.988	3.899	H	2.560	4.722	-0.611				
C	-2.309	6.406	2.669	H	2.255	5.482	1.742				

The postulated species responsible for the regio-selectivity observed for five-membered heterocycles have been modelled for imidazole. The namely the Ir(Bpin)₃(L)(imidazole) complex, was modelled with Spartan at the PM3-level of semi-empirical calculations (Figure S15). It shows that *beta*-C-H bond functionalization in the imidazole substrate is feasible. Importantly, the other heterocyclic protons are too far away from the iridium active site to be activated.

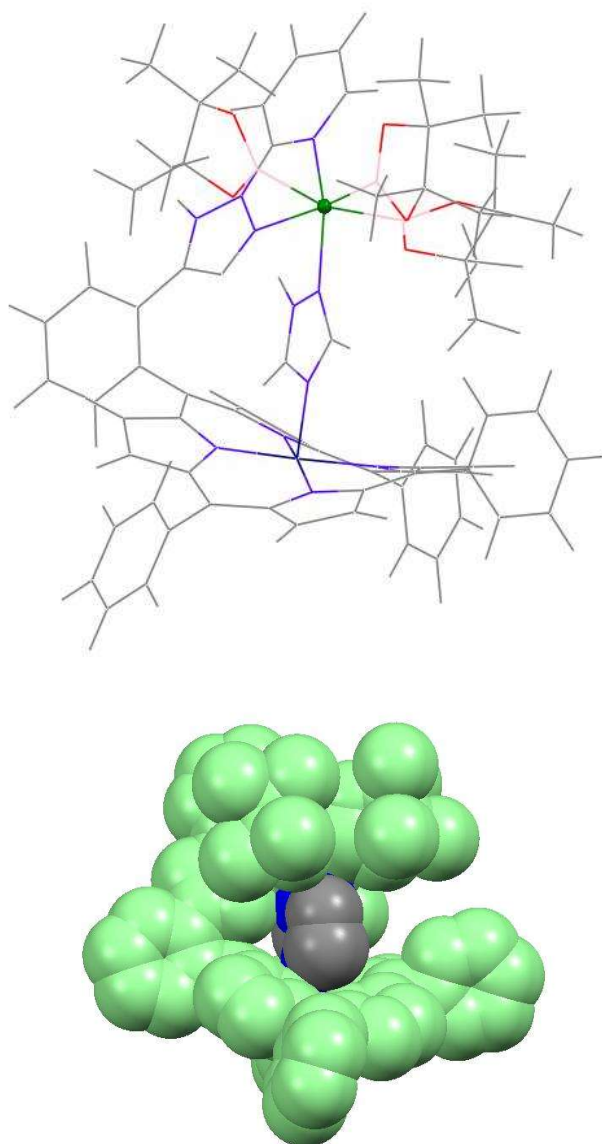
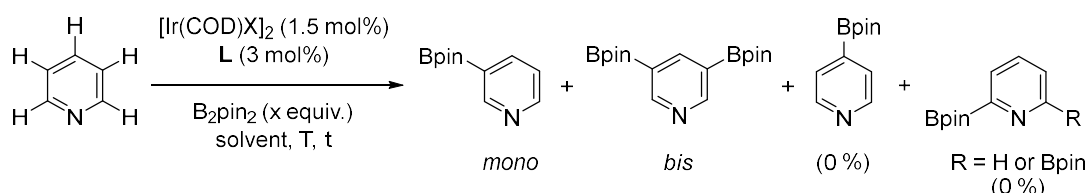


Figure S15. Molecular modelling (semi-empirical calculations) of the targeted supramolecular approach for pyridine functionalization. Top: wireframe representation, gray = carbon, blue = nitrogen, pink = boron, red = oxygen, green = iridium, dark blue = zinc. Bottom: van der Waals representation (hydrogen atoms omitted), green = catalyst, blue/gray = imidazole substrate.

N 2.280	-0.415	-3.748	C-3.156	3.149	3.102	H -7.295	4.695	-1.617
C 2.766	0.162	-4.874	C-3.311	5.685	4.132	C -5.368	2.619	-1.829
C 3.244	-0.558	2.803	C-3.930	3.348	4.234	H -4.378	2.258	-2.129
C 4.029	0.636	-4.555	C-2.545	5.422	2.996	H -6.017	2.630	-2.710
C 4.336	0.167	-3.255	C-4.004	4.641	4.750	H -5.760	1.876	-1.124
C 3.078	-1.434	-1.710	N-2.494	4.172	2.520	C -4.690	4.980	-3.503
C 1.875	-1.858	-1.274	Ir-1.371	3.652	0.773	H -4.375	4.016	-3.917
N 0.625	-1.550	-1.693	Zn 0.034	-0.565	-3.294	H -4.081	5.733	-4.017
C-0.235	-1.988	-0.774	H-3.781	1.597	-6.299	H -5.739	5.152	-3.761
C 0.445	-2.769	0.267	H-5.815	1.723	-7.703	C -4.642	6.492	-1.510
C 1.724	-2.687	-0.087	H 7.034	-0.345	-8.317	H -4.455	6.578	-0.433
C-1.678	-1.750	-0.684	H 6.219	-2.550	-7.530	H -5.645	6.874	-1.723
C-2.250	-1.211	-1.767	H-4.191	-2.699	-6.126	H -3.916	7.153	-1.996
N-1.716	-0.795	-2.971	H-4.468	2.537	4.717	O -1.302	6.763	0.010
C-2.704	-0.681	-3.927	H-4.605	4.840	5.639	N -0.519	5.584	0.257
C-3.700	-1.071	-1.919	H-3.367	6.695	4.534	O 0.895	5.819	0.108
C-3.966	-0.751	-3.191	H-1.982	6.180	2.471	C 1.005	7.263	0.014
C-2.640	-0.634	-5.261	H-1.912	-0.979	-8.052	C -0.366	7.689	-0.598
C-1.307	-0.704	-5.851	H 0.620	-0.563	-8.448	C -0.463	7.458	-2.113
N-0.129	-0.578	-5.239	H 2.093	2.340	-7.584	H -0.184	6.433	-2.381
C 0.804	-0.373	-6.200	H 3.360	2.782	-9.662	H 0.172	8.152	-2.671
C-1.157	-0.803	-7.308	H 4.821	1.028	-10.628	H -1.495	7.591	-2.459
C 0.142	-0.582	-7.480	H 5.022	-1.176	-9.515	C -0.802	9.113	-0.266
C 2.083	0.042	-6.103	H 3.767	-1.641	-7.437	H -1.775	9.335	-0.719
C 4.380	-0.409	-9.087	H 4.711	1.137	-5.233	H -0.078	9.849	-0.628
C 2.732	1.563	-7.996	H 5.296	0.253	-2.757	H -0.941	9.252	0.811
C 3.669	-0.668	-7.914	H 4.475	-3.716	-2.220	C 2.222	7.605	-0.840
C 4.267	0.831	-9.712	H 6.503	-4.532	-1.070	H 3.144	7.269	-0.352
C 3.445	1.817	-9.168	H 7.500	-3.223	0.781	H 2.299	8.682	-1.017
C 2.836	0.315	-7.363	H 6.473	-1.081	1.486	H 2.195	7.087	-1.805
C-5.459	0.759	-7.346	H 4.443	-0.243	0.347	C 1.227	7.764	1.449
C-4.541	-1.723	-6.458	H 2.527	-3.157	0.460	H 0.380	7.510	2.097
C-6.145	-0.403	-7.693	H 0.023	-3.292	1.106	H 1.381	8.847	1.482
C-4.313	0.684	-6.553	H -4.126	-1.807	3.394	H 2.104	7.281	1.894
C-3.848	-0.558	-6.104	H -4.535	-4.187	3.164	O 1.672	3.009	1.540
C-5.687	-1.644	-7.251	H -3.684	-5.430	1.197	N 0.340	3.202	2.028
C-2.484	-2.305	0.433	H -2.391	-4.258	-0.528	O 0.243	3.007	3.464
C-3.967	-3.667	2.395	H -4.443	-1.254	-1.158	C 1.623	2.894	3.896
C-2.759	-3.690	0.326	H -4.954	-0.637	-3.612	C 2.345	2.334	2.634
C-2.992	-1.577	1.536	O 0.053	1.569	-2.662	C 3.837	2.644	2.553
C-3.722	-2.295	2.511	C -0.979	1.978	-1.854	H 4.023	3.722	2.506
C-3.491	-4.364	1.298	C -0.409	2.832	-0.960	H 4.268	2.230	1.635
C 4.878	-1.186	0.035	O 0.916	2.976	-1.299	H 4.381	2.226	3.406
C 6.044	-3.596	-0.759	C 1.207	2.143	-2.307	C 2.115	0.831	2.405
C4.302	-1.927	-1.007	H 2.186	1.991	-2.727	H 2.664	0.221	3.128
C 6.025	-1.654	0.678	H -1.959	1.565	-1.964	H 2.433	0.544	1.397
C 6.605	-2.858	0.282	H 1.565	3.543	-0.764	H 1.052	0.573	2.467
C4.898	-3.132	-1.405	O -4.473	3.823	0.025	C 1.680	1.986	5.121
C-2.817	-0.127	1.708	B -3.133	4.094	-0.412	H 1.186	1.027	4.936
C-3.426	0.646	2.722	O -3.087	4.694	-1.715	H 1.142	2.438	5.963
H-4.089	0.407	3.540	C -4.466	5.046	-1.995	H 2.712	1.799	5.434
N-2.028	0.682	0.859	C -5.279	4.001	-1.167	C 2.062	4.314	4.282
N-2.179	1.874	1.363	C -6.673	4.459	-0.749	H 1.392	4.732	5.042
N-2.975	1.911	2.465	H -6.631	5.335	-0.093	H 2.009	4.995	3.425
			H -7.178	3.680	-0.165	H 3.082	4.330	4.679

5. Catalysis experiments.

5.1. General procedure: Iridium catalyst precursor, B₂pin₂, ligand **L**, and dodecane (4.05 x 10⁻⁵ mol, 0.25 equiv.) as the internal standard were introduced in an oven dried Schlenk flask. Solvent (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Next, pyridine (1.62 x 10⁻⁴ mol, 1 equiv.) was added and the reaction was stirred at a given temperature during a given time. Back at room temperature, the reactions were analyzed by GC-MS. The optimization study is provided in the Table S1 below:

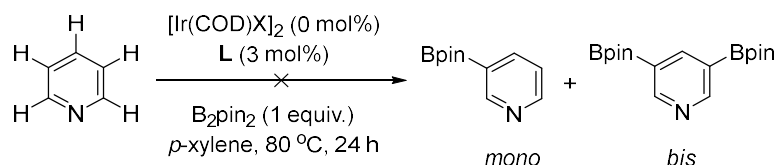


Entry	[Ir(COD)X] ₂	x	solvent	T (°C)	t (h)	conv. (%) ^[a]	yield (%) ^[b]	mono:bis ^[c]
1	X = Cl	1	heptane	80	48	<50	26	90:10
2	X = OMe	1	heptane	80	48	<25	16	100:0
3	X = OMe	1	heptane	80	72	<25	18	88:12
4	X = OMe	1	heptane	80	24	<25	10	100:0
5	X = Cl	1	DCE	70	48	<5	<5	-
6	X = Cl	1	THF	50	48	0	0	-
7	X = Cl	1	MTBE	80	48	<50	26	89:11
8	X = Cl	1	2-Me-THF	80	24	<25	12	100:0
9	X = Cl	1	2-Me-THF	80	72	<50	26	100:0
10	X = Cl	1	toluene	r.t.	24	0	0	-
11	X = OMe	1	toluene	r.t.	24	0	0	-
12	X = Cl	1	toluene	40	24	0	0	-
13	X = Cl	1	toluene	60	24	0	0	-
14	X = Cl	1	toluene	70	24	>99	60	90:10
15	X = Cl	1	toluene	80	24	>99	>99	25:75
16	X = Cl	1	<i>p</i> -xylene	80	24	>99	>99	40:60
17	X = OMe	1	<i>p</i> -xylene	80	24	>75	73	75:25
18	X = Cl	1	<i>p</i> -xylene	50	48	0	0	-
19	X = Cl	1.5	<i>p</i> -xylene	80	24	>99	84	25:75
20	X = Cl	0.5	<i>p</i> -xylene	80	24	<50	35	90:10
21	X = Cl	1	neat	80	24	<5	<5	-
22	X = Cl	1	<i>p</i> -xylene	90	24	>99	87	50:50
23	X = Cl	2	<i>p</i> -xylene	110	24	>99	63	50:50
24	X = Cl	1.5	toluene	70	24	>99	52	60:40
25	X = Cl	1	<i>p</i> -xylene	70	24	<50	45	83:17
26	X = Cl	2	<i>p</i> -xylene	100	24	>99	>99	33:67
27 ^[d]	X = Cl	1	<i>p</i> -xylene	80	24	>99	75	33:67
28	X = Cl	3	<i>p</i> -xylene	80	24	>99	75	33:67
29 ^[d]	X = Cl	3	<i>p</i> -xylene	80	48	>99	94	13:87

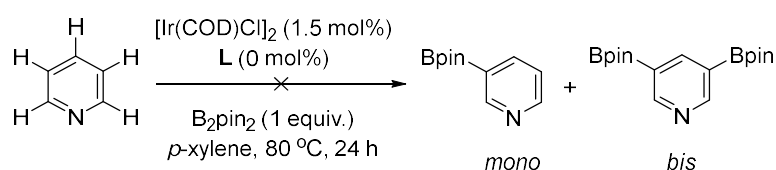
^[a]conversion of pyridine. ^[b]yield of products. ^[c]ratio of mono/bis-borylated products. ^[d]Ir precursor (3 mol%) and **L** (6 mol%).

5.2. Control experiments.

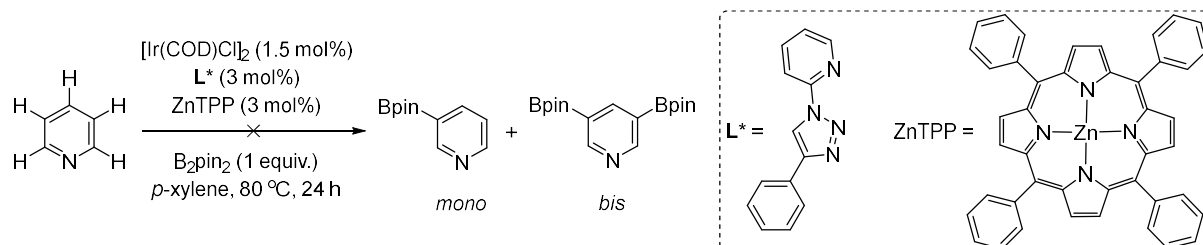
- **Control experiment without any iridium precursor:** B₂pin₂ (41.1 mg, 1.62 x 10⁻⁴ mol, 1 equiv.) Ligand L (4.1 mg, 4.9 x 10⁻⁶ mol, 0.03 equiv.) and dodecane (6.9 mg, 9.2 μL, 4.05 x 10⁻⁵ mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then, pyridine (13 mg, 13 μL, 1.62 x 10⁻⁴ mol, 1 equiv.) was added. The reaction mixture was stirred during 24 h at 80 °C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.



- **Control experiment without L:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 x 10⁻⁶, 0.015 equiv.), B₂pin₂ (41.1 mg, 1.62 x 10⁻⁴ mol, 1 equiv.) and dodecane (6.9 mg, 9.2 μL, 4.05 x 10⁻⁵ mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then pyridine (13 mg, 13 μL, 1.62 x 10⁻⁴ mol, 1 equiv.) was added. The reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.

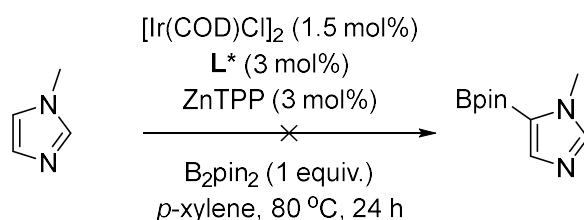


- **Control experiment using ligand L* + ZnTPP:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 x 10⁻⁶ mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62 x 10⁻⁴ mol, 1 equiv.), ligand L* (1.1 mg, 4.9 x 10⁻⁶ mol, 0.03 equiv.), ZnTPP (3.3 mg, 4.9 x 10⁻⁶ mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μL, 4.05 x 10⁻⁵ mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then pyridine (13 mg, 13 μL, 1.62 x 10⁻⁴ mol, 1 equiv.) was added. The reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.



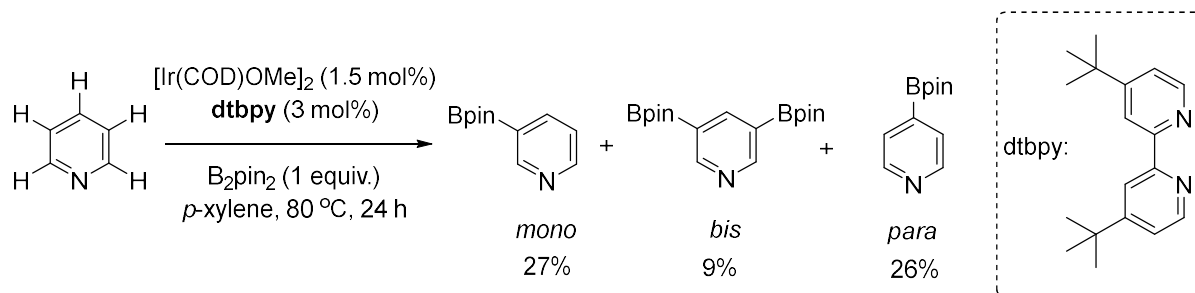
- **Control experiment for *N*-methyl imidazole borylation using ligand L* + ZnTPP:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 x 10⁻⁶ mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62 x 10⁻⁴ mol, 1 equiv.),

ligand **L*** (1.1 mg, 4.9×10^{-6} mol, 0.03 equiv.), ZnTPP (3.3 mg, 4.9×10^{-6} mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μ L, 4.05×10^{-5} mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then *N*-methylimidazole (13.5 mg, 13 μ L, 1.62×10^{-4} mol, 1 equiv.) was added. The reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.

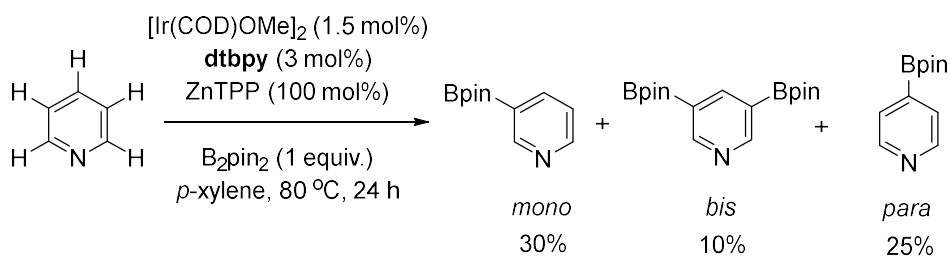


Using ZnTPP as a hindered lewis acid:

- **Standard reaction using [Ir(dtbpv)] complex as the catalyst:** [Ir(COD)(OMe)]₂ (1.6 mg, 2.4×10^{-6} mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), dtbpv (1.3 mg, 4.9×10^{-6} mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μ L, 4.05×10^{-5} mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then pyridine (13 mg, 13 μ L, 1.62×10^{-4} mol, 1 equiv.) was added. The reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing a quantitative conversion and a mixture of products *meta* (27% mono-borylated and 9% bis-borylated) and *para* (26%) substituted.

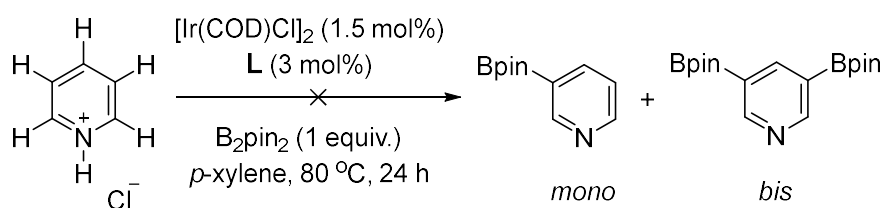


- **Borylation using ZnTPP as an hindered lewis acid:** [Ir(COD)(OMe)]₂ (1.6 mg, 2.4×10^{-6} mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), dtbpv (1.3 mg, 4.9×10^{-6} mol, 0.03 equiv.), ZnTPP (55.5 mg, 1.62×10^{-4} mol, 1 equiv.), and dodecane (6.9 mg, 9.2 μ L, 4.05×10^{-5} mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then pyridine (13 mg, 13 μ L, 1.62×10^{-4} mol, 1 equiv.) was added. The reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing a quantitative conversion and a mixture of products *meta* (30% mono-borylated and 10% bis-borylated) and *para* (25%) substituted.

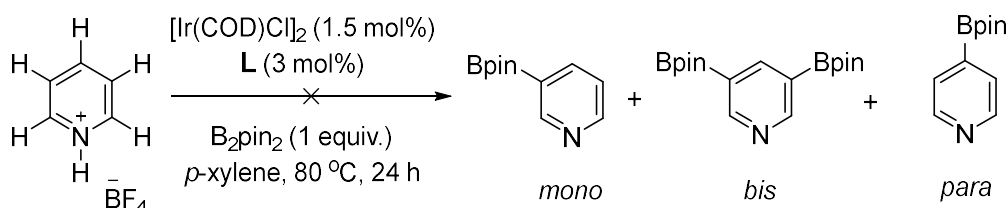


These results show that ZnTPP is not bulky enough to induce a regioselective *para*-borylation of pyridine using this reaction conditions.

- **Control experiment using pyridinium chloride instead of pyridine as the substrate:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 × 10⁻⁶ mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62 × 10⁻⁴ mol, 1 equiv.), ligand **L** (4.1 mg, 4.9 × 10⁻⁶ mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μL, 4.05 × 10⁻⁵ mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then pyridinium chloride (19 mg, 1.62 × 10⁻⁴ mol, 1 equiv.) was added and the reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.

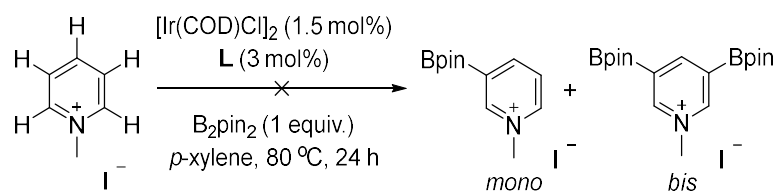


- **Control experiment using pyridinium tetrafluoroborate instead of pyridine as the substrate:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 × 10⁻⁶ mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62 × 10⁻⁴ mol, 1 eq.), ligand **L** (4.1 mg, 4.9 × 10⁻⁶ mol, 0.03 eq.), pyridinium tetrafluoroborate (27 mg, 1.62 × 10⁻⁴ mol, 1eq.) and dodecane (6.9 mg, 9.2 μL, 4.05 × 10⁻⁵ mol, 0.25 eq.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes and at 80°C for 24 hours. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.

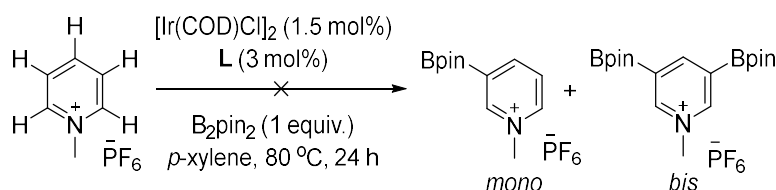


- **Control experiment using N-methylpyridinium iodide instead of pyridine as the substrate:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 × 10⁻⁶ mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62 × 10⁻⁴ mol, 1 equiv.), ligand **L** (4.1 mg, 4.9 × 10⁻⁶ mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μL, 4.05 × 10⁻⁵ mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then *N*-

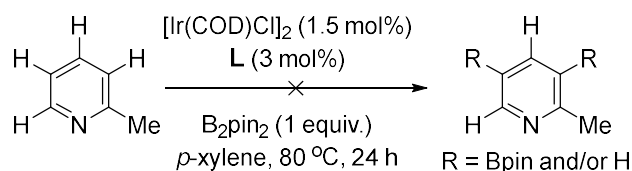
methylpyridinium iodide (36 mg, 1.62×10^{-4} mol, 1 equiv.) was added and the reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.



- **Control experiment using *N*-methylpyridinium hexafluorophosphate instead of pyridine as the substrate:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4×10^{-6} mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), ligand L (4.1 mg, 4.9×10^{-6} mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μL, 4.05×10^{-5} mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then *N*-methylpyridinium hexafluorophosphate (39 mg, 1.62×10^{-4} mol, 1 equiv.) was added and the reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.

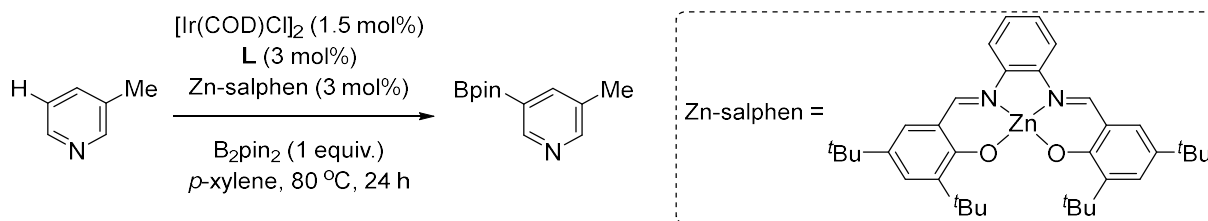


- **Control experiment using 2-methylpyridine as the substrate:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4×10^{-6} mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), ligand L (4.1 mg, 4.9×10^{-6} mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μL, 4.05×10^{-5} mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then 2-methylpyridine (15 mg, 16 μL, 1.62×10^{-4} mol, 1 equiv.) was added and the reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing no conversion of starting materials nor product formation.

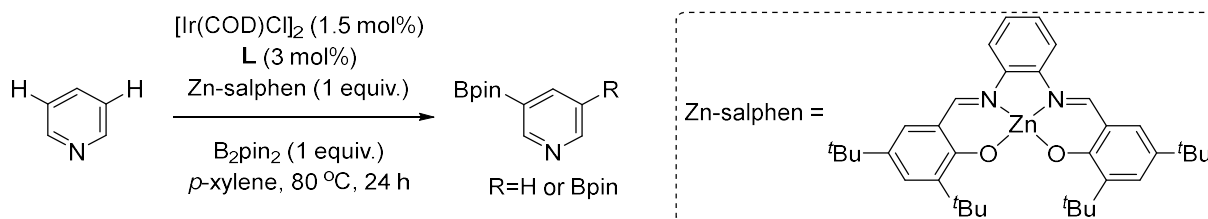


- **Competition between ligand L and zinc(II)-salphen using a pyridine-type substrate:** [Ir(COD)(Cl)]₂ (1.7 mg, 2.4×10^{-6} mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), ligand L (4.1 mg, 4.9×10^{-6} mol, 0.03 equiv.) and Zn(II)-salphen (2.9 mg, 4.9×10^{-6} mol, 0.03 equiv.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then 3-methylpyridine (15 mg, 16 μL, 1.62×10^{-4} mol, 1 equiv.) was added and the reaction mixture was stirred during 24

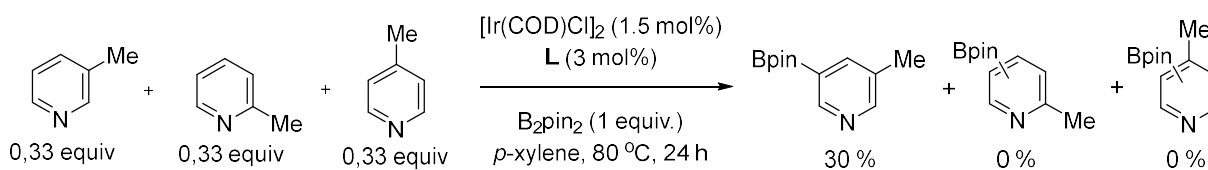
h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing 53% conversion and an estimated GC-yield of 47%. *This indicates that the zinc(II)-salphen competes with the ligand to bind to the substrate, thus leading to a decrease in the catalytic activity.*



$[\text{Ir}(\text{COD})(\text{Cl})]_2$ (1.7 mg, 2.4×10^{-6} mol, 0.015 eq.), B_2pin_2 (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), ligand L (4.1 mg, 4.9×10^{-6} mol, 0.03 equiv.) and $\text{Zn}(\text{II})\text{-salphen}$ (97.9 mg, 1.62×10^{-4} mol, 1 equiv.) were introduced in an oven dried Schlenk flask. $p\text{-xylene}$ (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then pyridine (13 mg, 13 μL , 1.62×10^{-4} mol, 1 equiv.) was added and the reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing conversion <5% and traces amount of product. *This indicates that the zinc(II)-salphen likely binds quantitatively to the substrate in a equimolar ratio thus leading to almost no catalytic activity.*



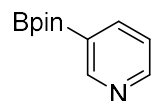
- **Competition between different pyridine substrates:** $[\text{Ir}(\text{COD})(\text{Cl})]_2$ (1.7 mg, 2.4×10^{-6} mol, 0.015 eq.), B_2pin_2 (41.1 mg, 1.62×10^{-4} mol, 1 equiv.), ligand L (4.1 mg, 4.9×10^{-6} mol, 0.03 equiv.), and dodecane (6.9 mg, 9.2 μL , 4.05×10^{-5} mol, 0.25 equiv.) were introduced in an oven dried Schlenk flask. $p\text{-xylene}$ (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then 2-Me-pyridine (5 mg, 5.3 μL , 0.53×10^{-5} mol, 1 equiv.), 3-Me-pyridine (5 mg, 5.3 μL , 0.53×10^{-5} mol, 1 equiv.) and 4-Me-pyridine (5 mg, 5.3 μL , 0.53×10^{-5} mol, 1 equiv.) were added and the reaction mixture was stirred during 24 h at 80°C. The reaction was cooled down to room temperature and analyzed by GC-MS analysis showing full conversion of 3-methylpyridine substrate as well as an estimated yield (based on B_2pin_2) of 30% of borylated product and no conversion of 2-methylpyridine nor 4-methylpyridine.

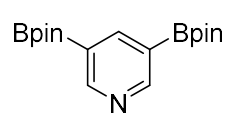


5.3. Dormant reactivity using pyridinium tetrafluoroborate as the substrate.

-Dormant reactivity procedure: $[\text{Ir}(\text{COD})(\text{Cl})_2]$ (1.7 mg, 2.4×10^{-6} mol, 0.015 eq.), B_2pin_2 (41.1 mg, 1.62×10^{-4} mol, 1 eq.), ligand **L** (4.1 mg, 4.9×10^{-6} mol, 0.03 eq.), pyridinium tetrafluoroborate (27 mg, 1.62×10^{-4} mol, 1eq.) and dodecane (6.9 mg, 9.2 μL , 4.05×10^{-5} mol, 0.25 eq.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. The reaction mixture was heated up to 80°C for 3 hours, and DIPEA (21 mg, 1.62×10^{-4} mol, 28 μL , 1eq.) was added. After 13 hours, the crude mixture was allowed to cool down to room temperature. A conversion of 90% was estimated by GC-MS analysis.

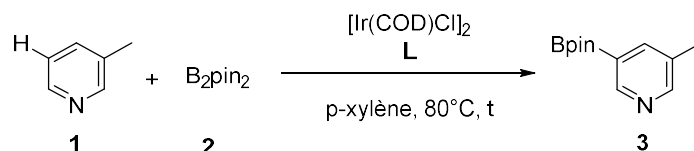
5.4. Characterization of the products formed in the reaction optimization.

 **3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (1):** Following the optimized conditions (Table 1, entry 14), full conversion and 54% yield was estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (16 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.95 (s, 1H), 8.67 (d, J = 2 Hz, 1H), 8.07 (dt, J = 7.6, 2 Hz, 1H), 7.26-7.32 (m, 1H), 1.38 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 155.44, 151.94, 142.22, 123.06, 84.23, 24.86 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ = 30.86 (s) ppm. The spectral data match those found in literature.^[9]

 **3,5-bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (2):** Following the optimized conditions (Table 1, entry 29), full conversion and 81% yield was estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (37mg, 70% yield). ^1H NMR (400 MHz, CDCl_3): δ = 9.00 (d, J = 1.9 Hz, 1H), 8.48 (t, J = 1.9 Hz, 1H), 1.35 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ = 157.50, 148.78, 84.18, 24.85 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ = 31.15 (s) ppm. The spectral data match those found in literature.^[10]

5.4. Kinetic study following reaction progress kinetic analysis.^[11]

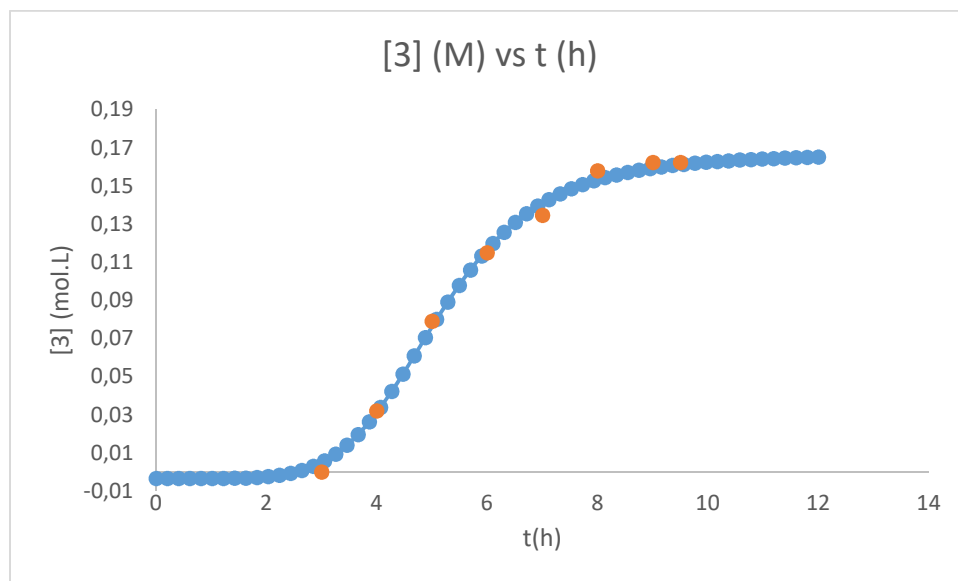
General procedure: $[\text{Ir}(\text{COD})(\text{Cl})_2]$, ligand **L**, B_2pin_2 , and dodecane (0.25 eq.) were introduced in an oven dried Schlenk flask. *p*-xylene was added and the reaction mixture was stirred at room temperature for 30 minutes. Then 3-methylpyridine was added and the mixture was stirred at 80°C. Small aliquots were taken from the flask under argon flow every hour using a dry needle. Conversion and yield were estimated by GC-MS using dodecane as the internal standard. Fitting of the experimental data was done using sigmoidal Boltzmann function.



5.4.1. Reaction at standard conditions.

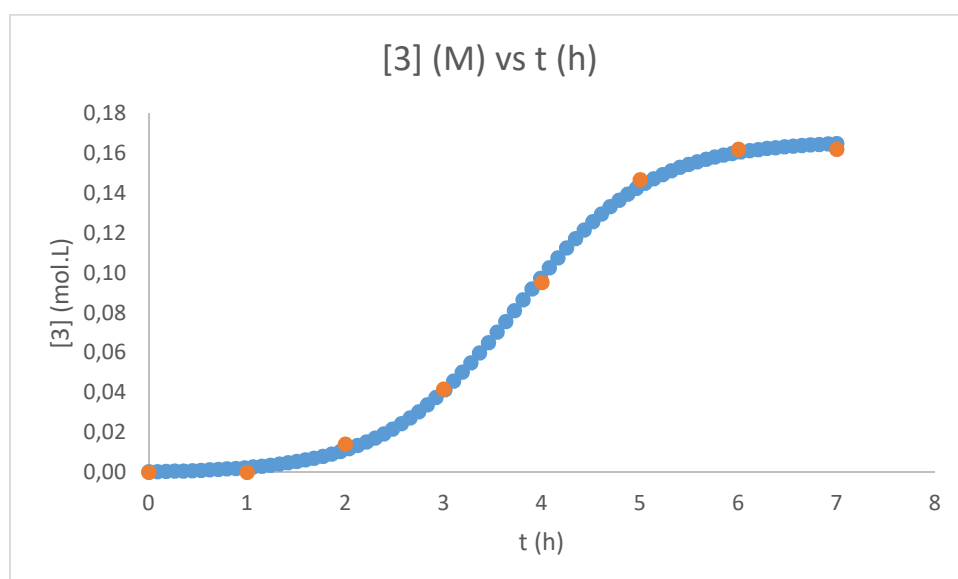
Following the general procedure, $[\text{Ir}(\text{COD})(\text{Cl})_2]$ (16.5 mg, 2.43×10^{-5} mol, 0.015 eq.), ligand **L** (41 mg, 4.86×10^{-5} mol, 0.03 eq.), B_2pin_2 (411 mg, 1.62×10^{-3} mol, 1 eq.) and 3-methylpyridine (160 μL , 1.62×10^{-3} mol, 1 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was

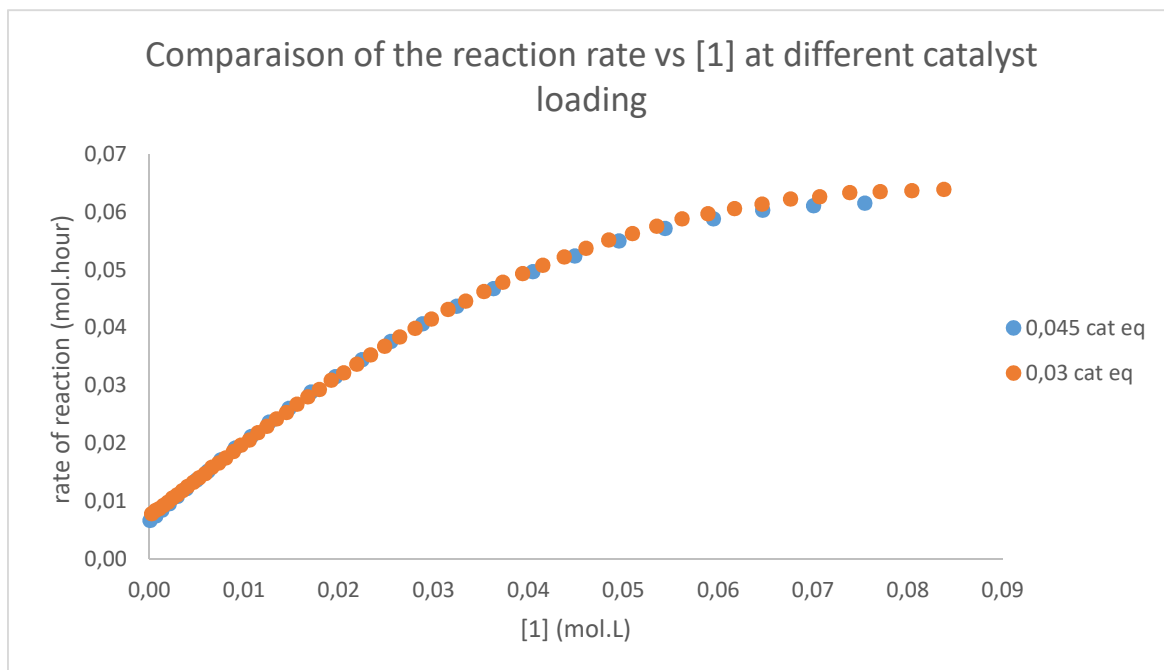
stirred at 80°C for 12 hours. Formation of *meta*-borylated product [3] versus time (h) is plotted below (fitted values are shown in bleu, and experimental values are shown in orange dots):



5.4.2. Reaction at different catalyst loading: determination of the catalyst kinetic order.

Following the general procedure, $[\text{Ir}(\text{COD})(\text{Cl})]_2$ (25 mg, 3.65×10^{-5} mol, 0.0225 eq.), ligand **L** (61.5 mg, 7.29×10^{-5} mol, 0.045 eq.), B_2pin_2 (411 mg, 1.62×10^{-3} mol, 1 eq.) and 3-methylpyridine (160 μL , 1.62×10^{-3} mol, 1 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was stirred at 80°C for 7 hours. Formation of *meta*-borylated product [3] versus time (h) is plotted below (fitted values are shown in bleu, and experimental values are shown in orange dots):





If the reaction is first order in catalyst, then the rate is directly related to the catalyst concentration following this formula:

$$\text{Rate} = k \times [\text{catalyst}]$$

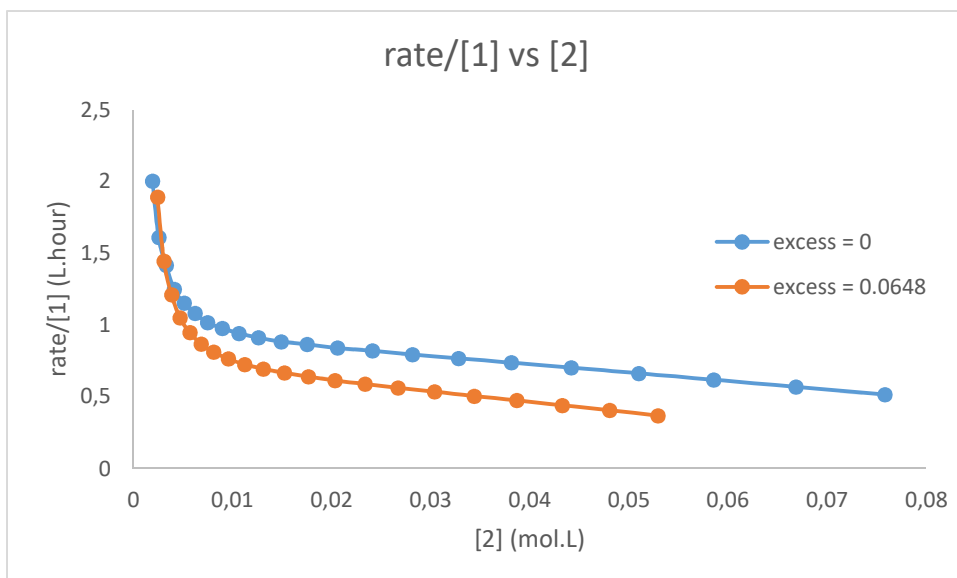
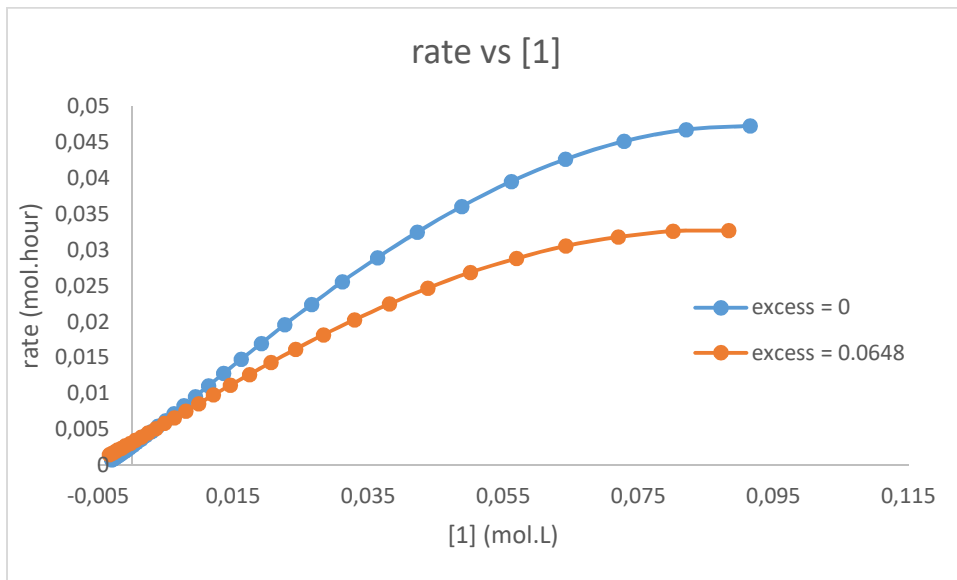
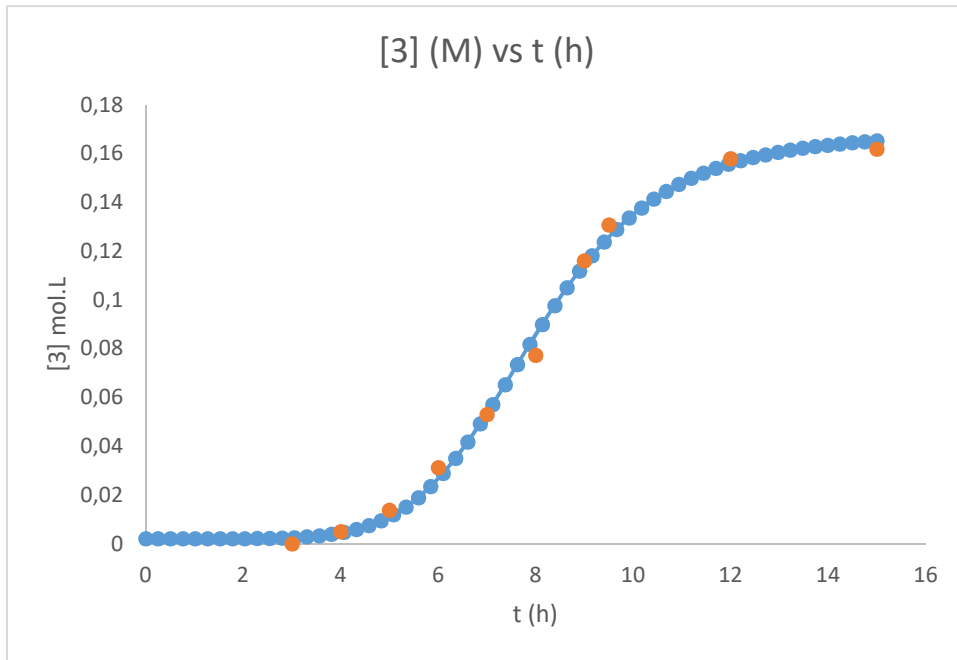
$$\text{Then: Rate}(\text{reaction1}) = \text{Rate}(\text{reaction2}) \times (\text{catalyst excess})$$

Overlapping of the two curves upon multiplication of the brown curve reaction rate by the catalyst excess (1.5) indicate a first order in catalyst.^[11]

5.4.3. Reaction at same excess: determination of the substrates kinetic order.

A. 1 equivalent of **1** and 0.6 equivalent of **2**.

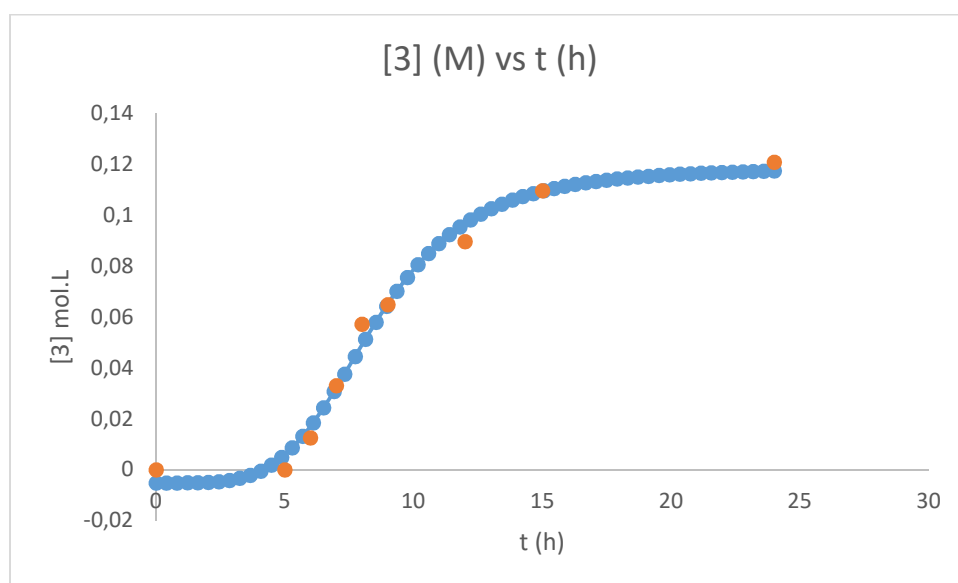
Following the general procedure, $[\text{Ir}(\text{COD})(\text{Cl})]_2$ (16.5 mg, 2.43×10^{-5} mol, 0.015 eq.), ligand **L** (41 mg, 4.86×10^{-5} mol, 0.03 eq.), B_2pin_2 (247 mg, 0.972×10^{-4} mol, 0.6 eq.) and 3-methylpyridine (160 μL , 1.62×10^{-3} mol, 1 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was stirred at 80°C and followed on time. Formation of *meta*-borylated product **[3]** versus time (h) is plotted below (fitted values are shown in bleu, and experimental values are shown in orange dots):



Following Blackmond's rules,^[11] the graphical data above suggests a pseudo-zero-order in B_2pin_2 as the curves are almost overlapping in the former case and very non-overlapping was observed for a pseudo-first order.

B. 0.8 equivalent of **1** and 0.4 equivalent of **2**.

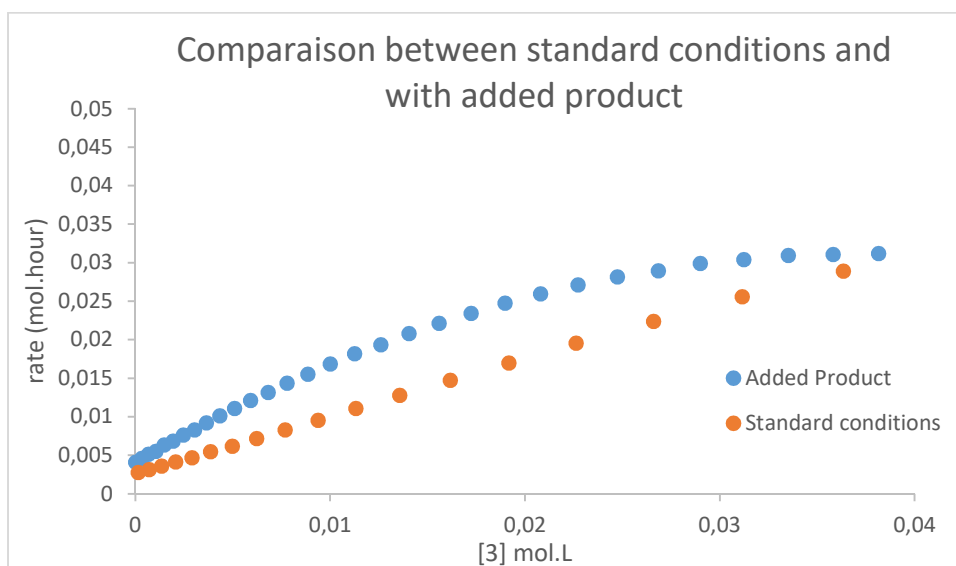
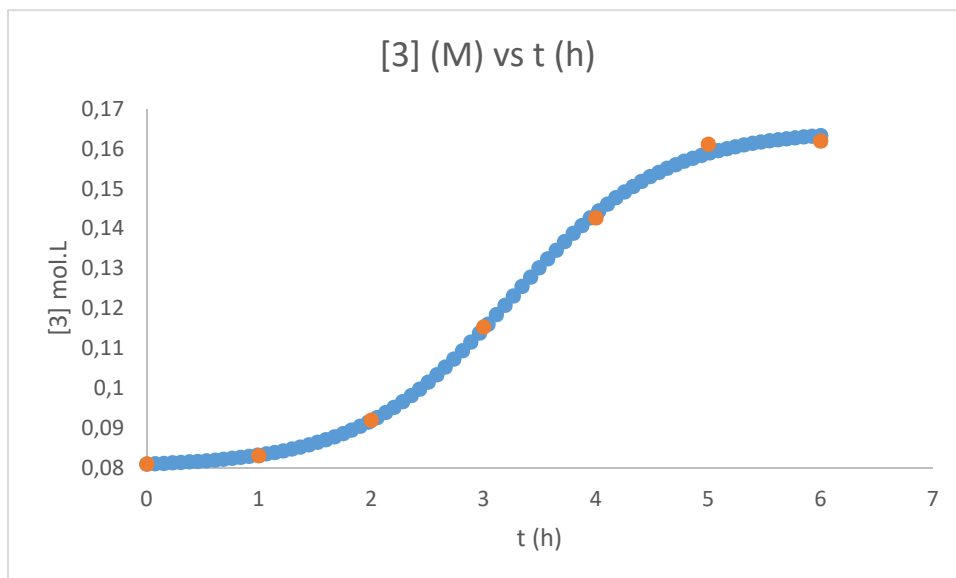
Following the general procedure, $[Ir(COD)(Cl)]_2$ (16.5 mg, 2.43×10^{-5} mol, 0.015 eq.), ligand **L** (41 mg, 4.86×10^{-5} mol, 0.03 eq.), B_2pin_2 (164 mg, 0.648×10^{-4} mol, 0.4 eq.) and 3-methylpyridine (128 μ L, 1.3×10^{-3} mol, 0.8 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was stirred at 80°C for 24 hours. Formation of *meta*-borylated product **[3]** versus time (h) is plotted below (fitted values are shown in bleu, and experimental values are shown in orange dots):



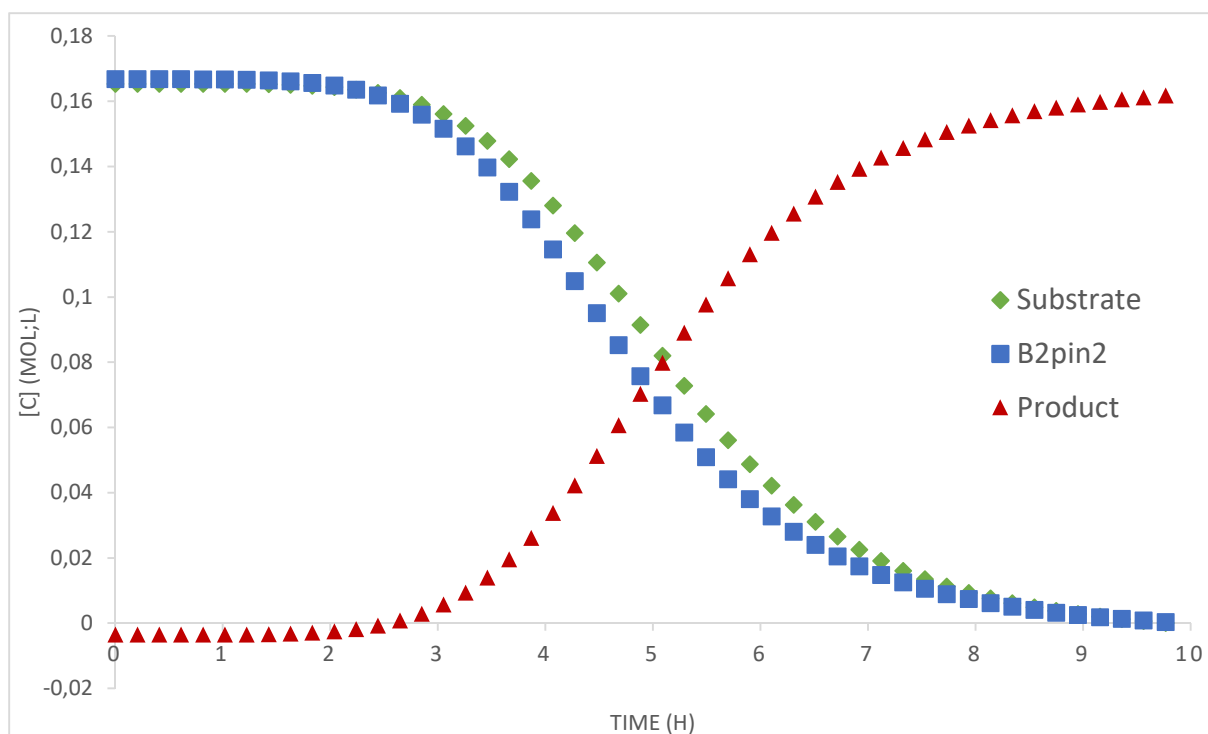
Note: a side-product from decomposition of B_2pin_2 is also likely a borylating agent as almost 2 equivalents of product relative to B_2pin_2 are generated. However, the kinetic data suggest that this side-product is less active than the starting reagent B_2pin_2 as the reaction appears to be slower upon total consumption of B_2pin_2 .

5.4.4. Reaction with added product: determination of product inhibition or catalyst deactivation.

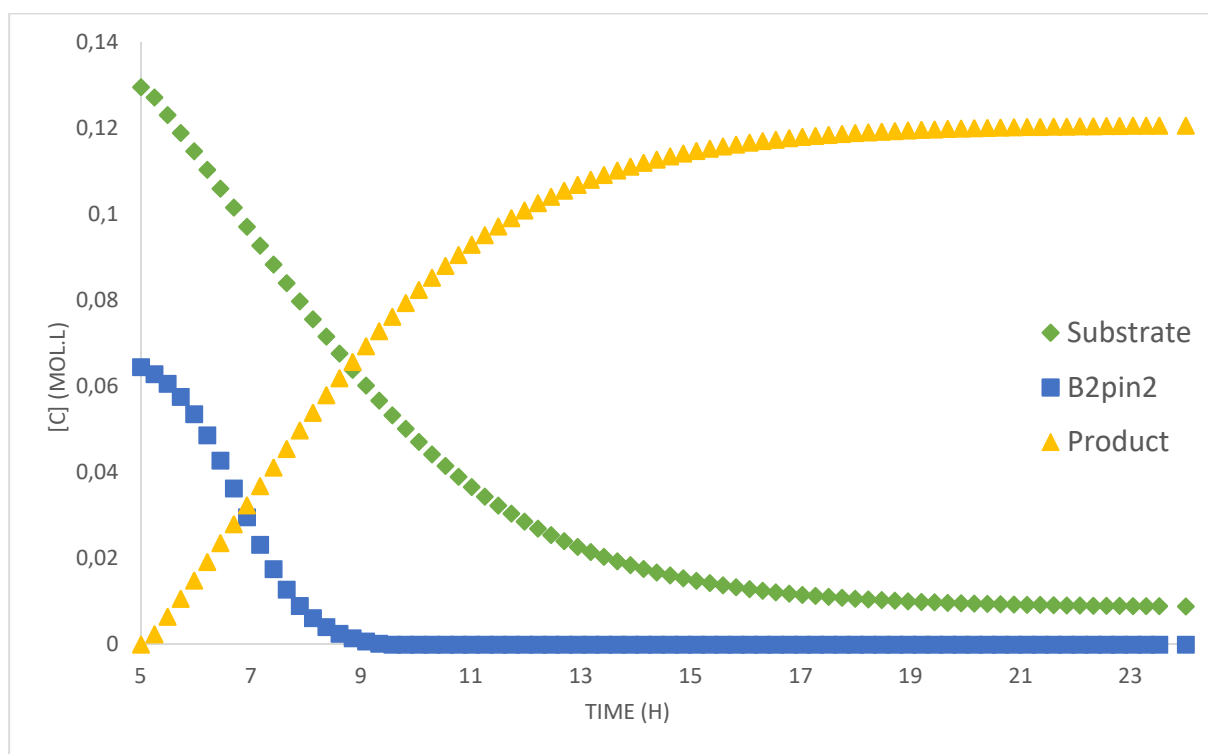
Following the general procedure, $[Ir(COD)(Cl)]_2$ (16.5 mg, 2.43×10^{-5} mol, 0.015 eq.), ligand **L** (41 mg, 4.86×10^{-5} mol, 0.03 eq.), B_2pin_2 (205.5 mg, 0.81×10^{-3} mol, 0.5 eq.), 3-methylpyridine (80 μ L, 0.81×10^{-3} mol, 0.5 eq.), and 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylpyridine (175 mg, 0.81×10^{-3} mol, 0.5 eq.) were dissolved in *p*-xylene (10 mL). The reaction mixture was stirred at 80°C for 6 hours. Formation of newly *meta*-borylated product **[3]** versus time (h) is plotted below (fitted values are shown in bleu, and experimental values are shown in orange dots):



Because there is no overlapping, product inhibition is very unlikely in the present case. Indeed, the reaction with added product (blue dots) is faster than the reaction under standard conditions (orange dots) which indicate that the catalyst is deactivated during the course of the reaction. We assume catalyst deactivation due to (multiple) borylation on the ligand or other type of chemical degradation/modification.



Kinetic profile for the C-H bond *meta*-borylation of 3-methylpyridine under standard conditions.

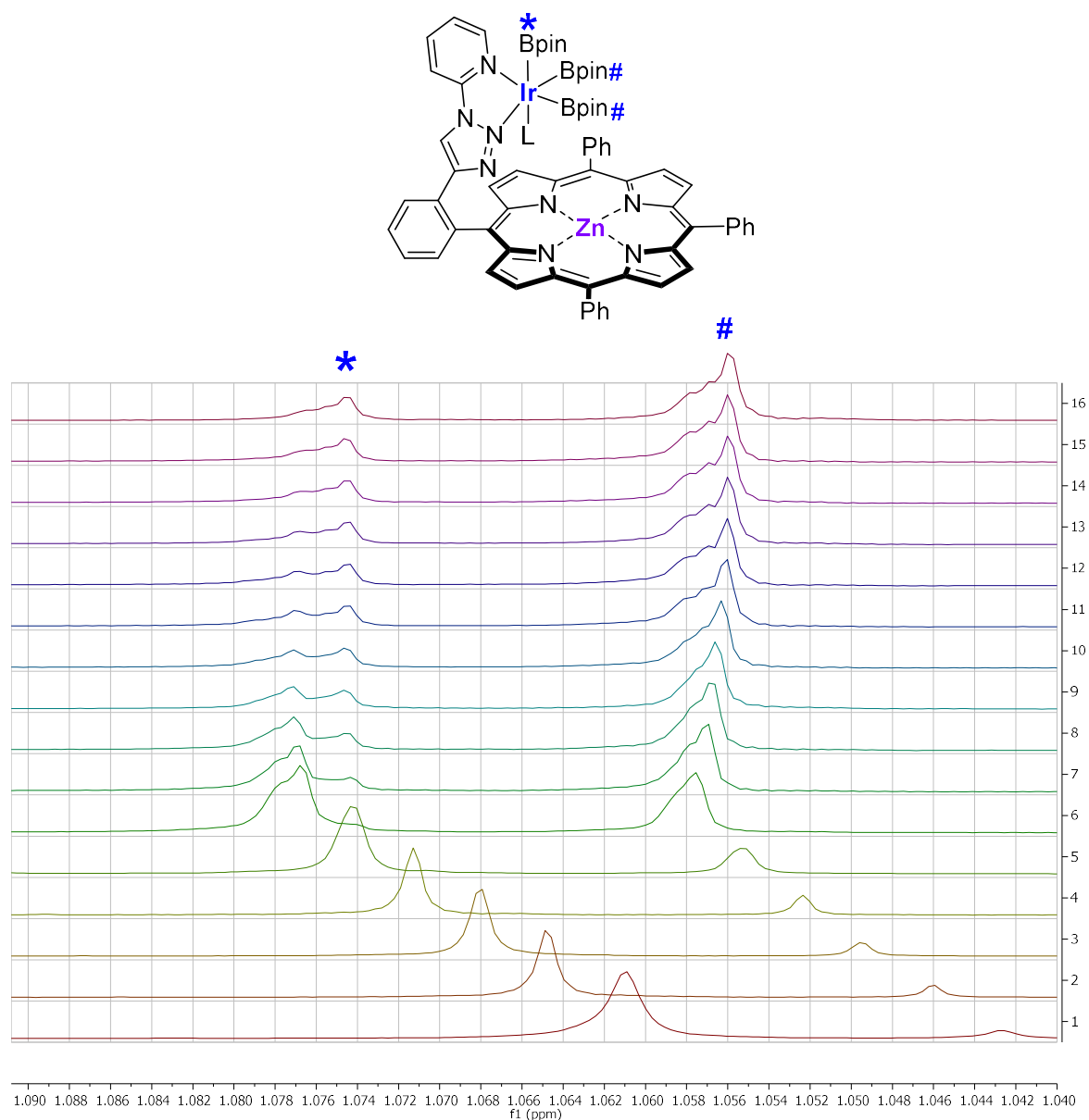


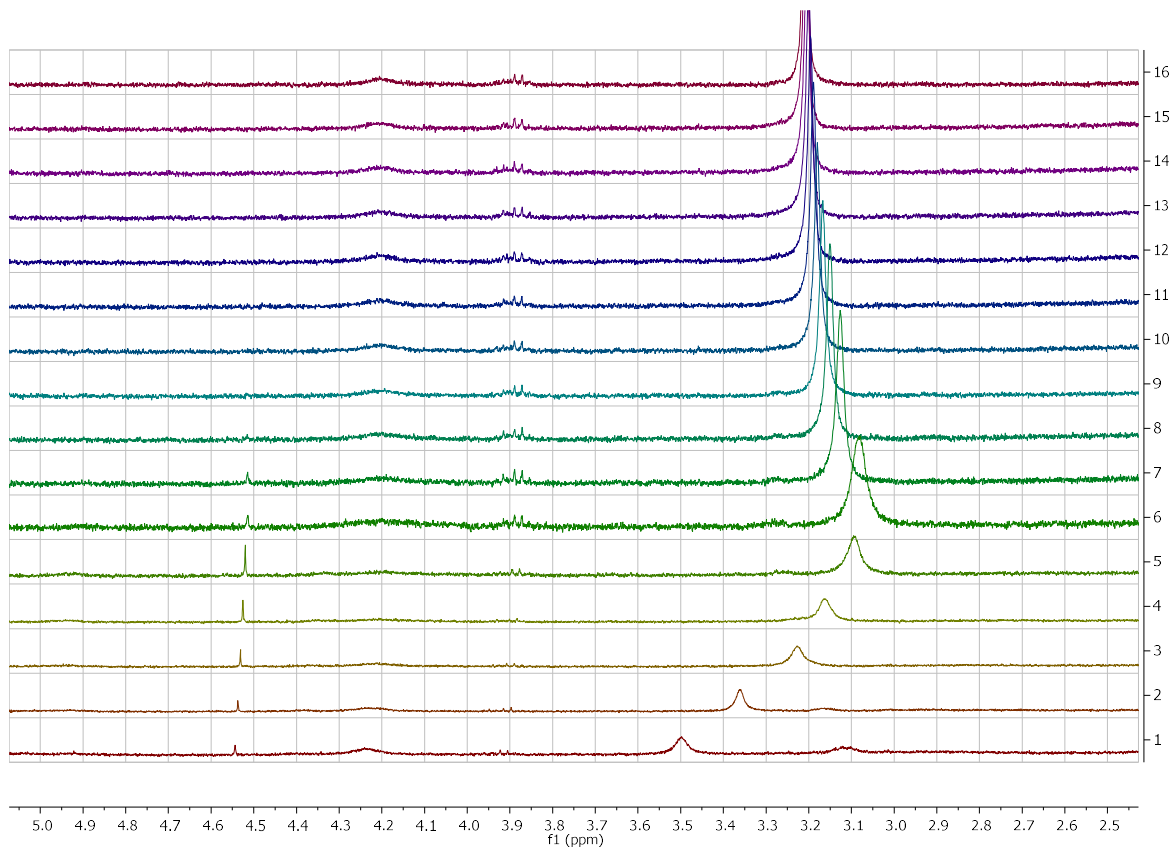
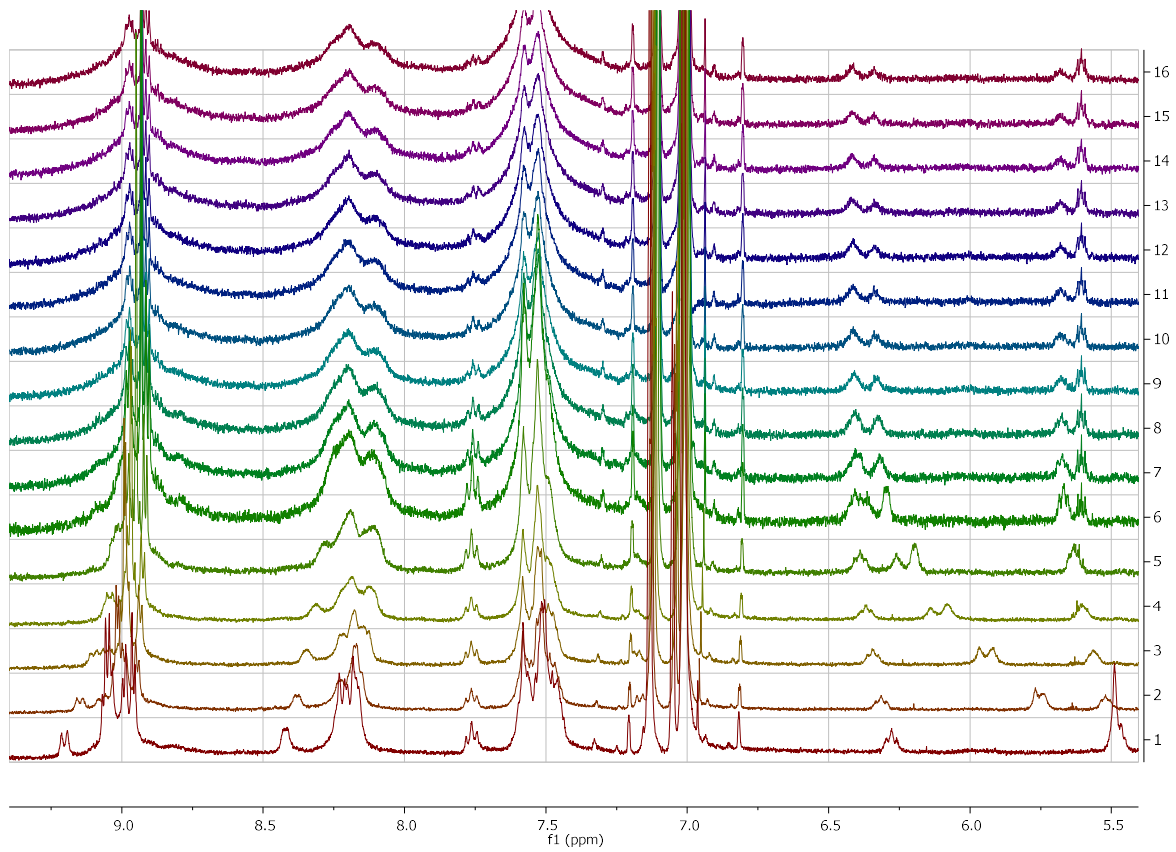
Kinetic profile for the C-H bond *meta*-borylation of 3-methylpyridine under conditions **B**.

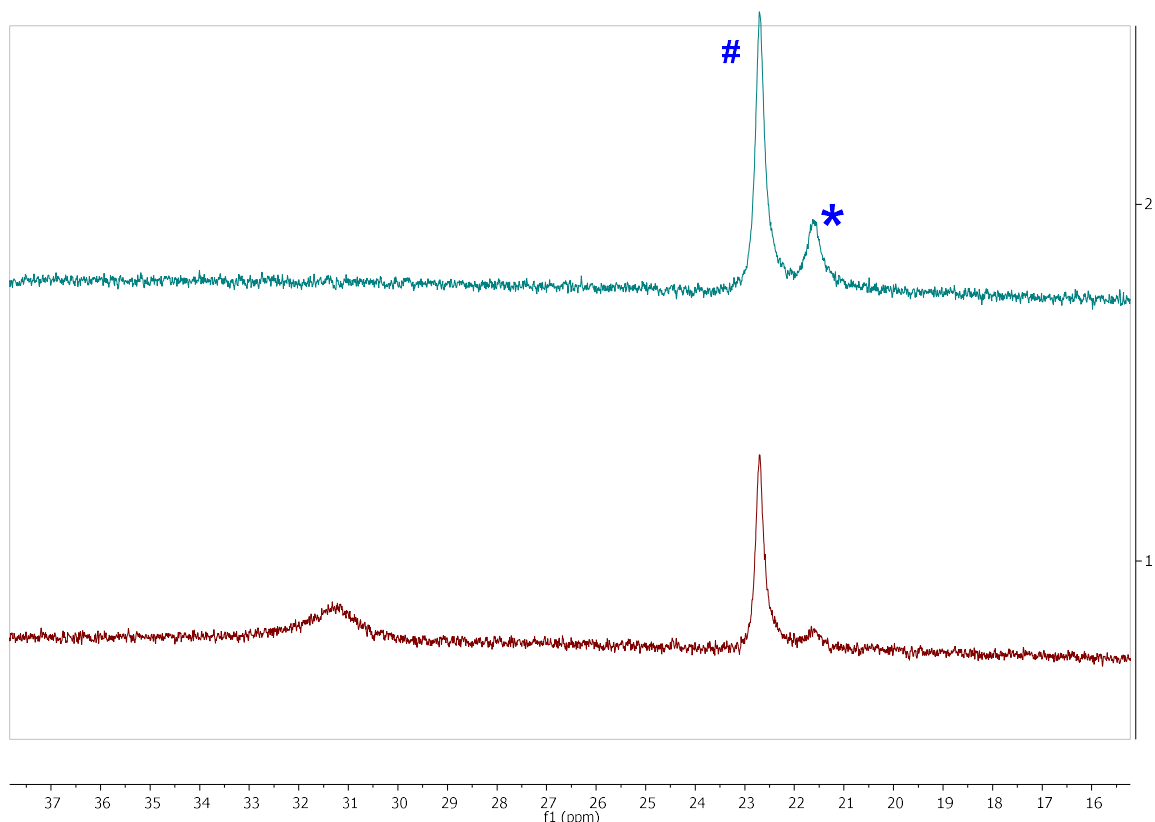
6. Identification of reaction intermediates.

6.1. High temperature ^1H and ^{11}B NMR study of the active catalyst formation: $[\text{Ir}(\text{Bpin})_3]\text{L}$:

Procedure for ^1H NMR follow-up of the borylation reaction: $[\text{Ir}(\text{COD})(\text{Cl})_2]$ (2 mg, 3.0×10^{-6} mol, 0.5 eq.), B_2pin_2 (4.63 mg, 1.83×10^{-5} mol, 3 eq.), and ligand **L** (5 mg, 6.1×10^{-6} mol, 1 eq) were introduced in an oven dried NMR tube. Deuterated toluene (1 mL) was added inside the NMR tube under argon atmosphere. The reaction mixture was analyzed every five minutes for 24 hours by ^1H NMR at 80°C . The below-presented ^1H NMR spectrum from bottom to top: r.t to 80°C (1 to 6) then every 2.4 hours at 80°C (6 to 16):





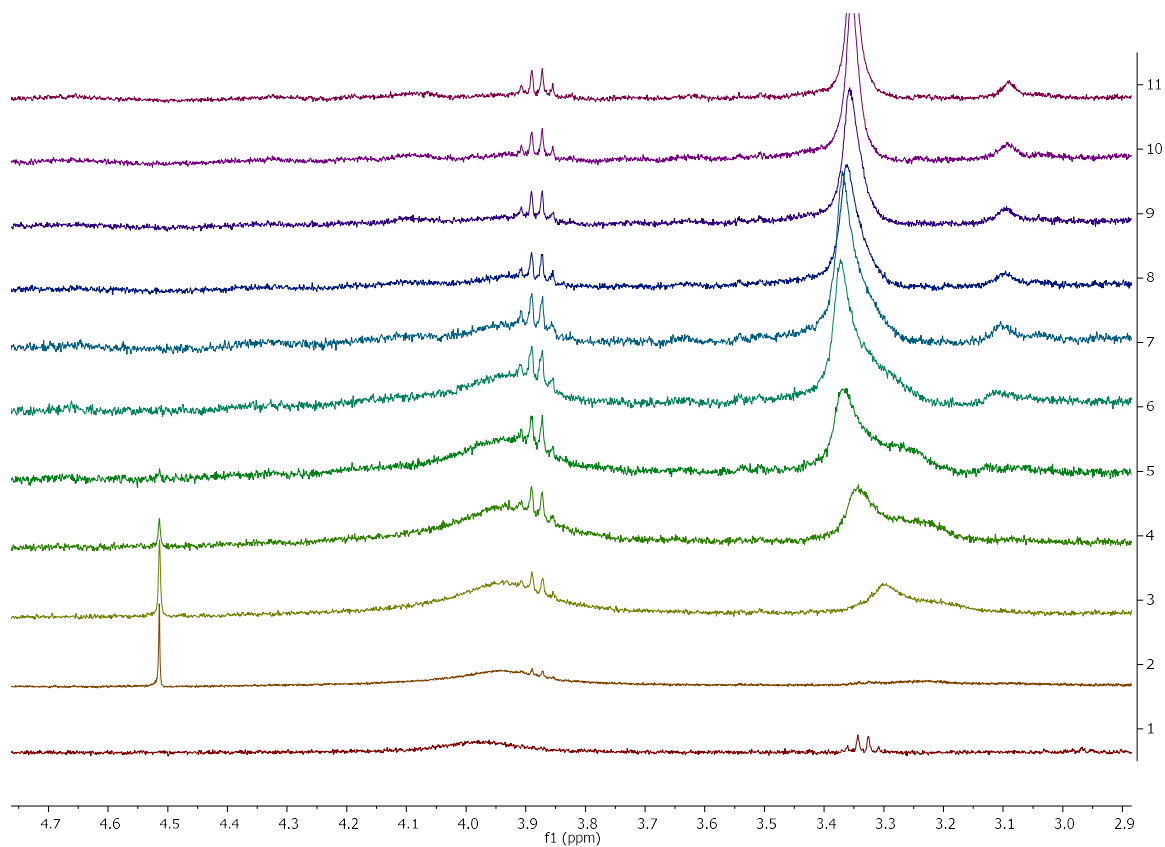


^{11}B NMR experiment: from 80°C at $t_{0\text{h}}$ to 80°C at $t_{24\text{h}}$ (bottom to top).

The above experiments indicate formation of the catalytically active $\text{L}(\text{Bpin})_3$ species at 80 °C with two set of peaks in the ^1H and ^{11}B NMR spectra while the COD ligand seems to de-coordinate the iridium center (a chemical shift in ^1H NMR from 3.5 to 3.15 ppm at 80 °C).

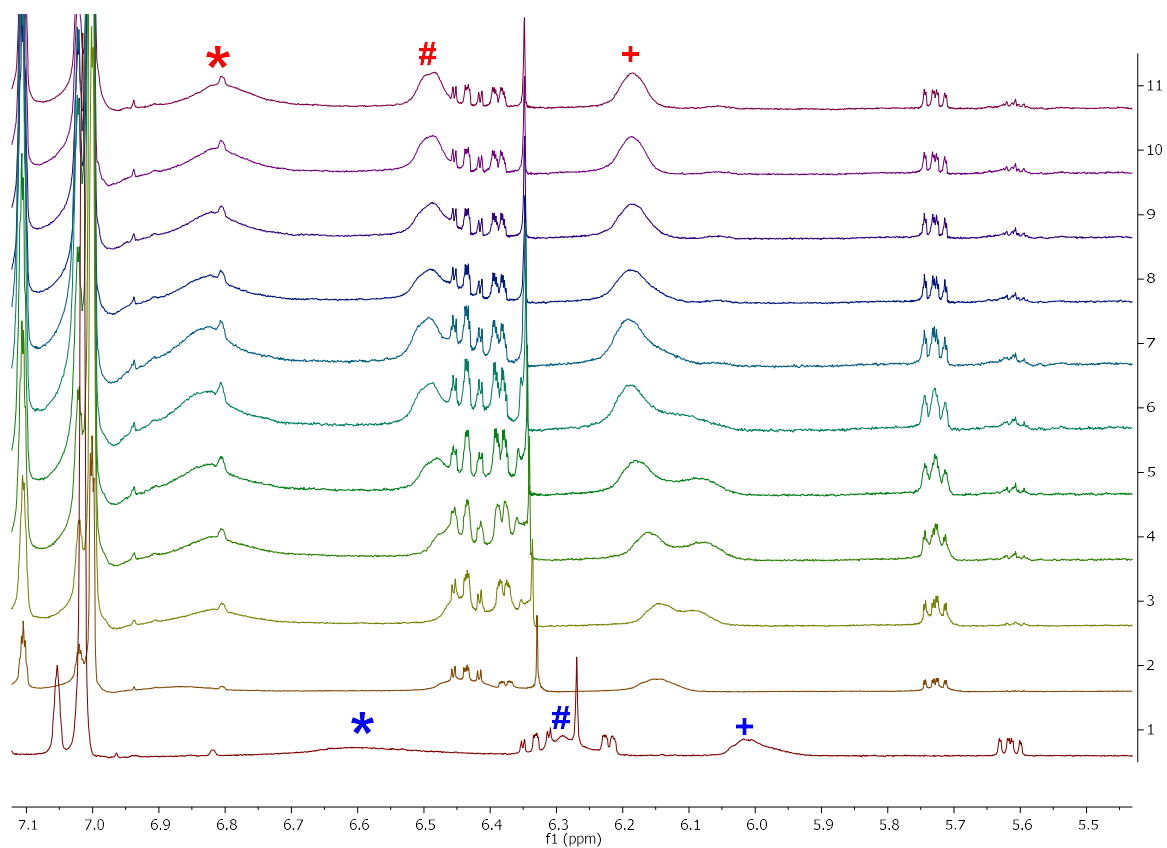
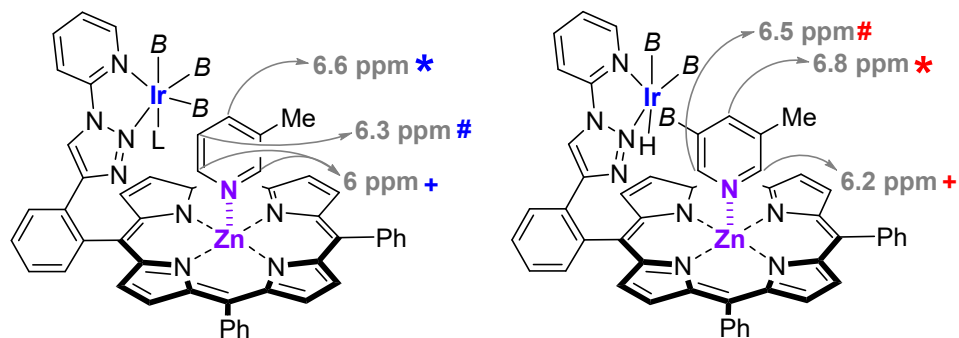
6.2. High temperature ^1H NMR study for the *meta*-C-H bond borylation of 3-methylpyridine.

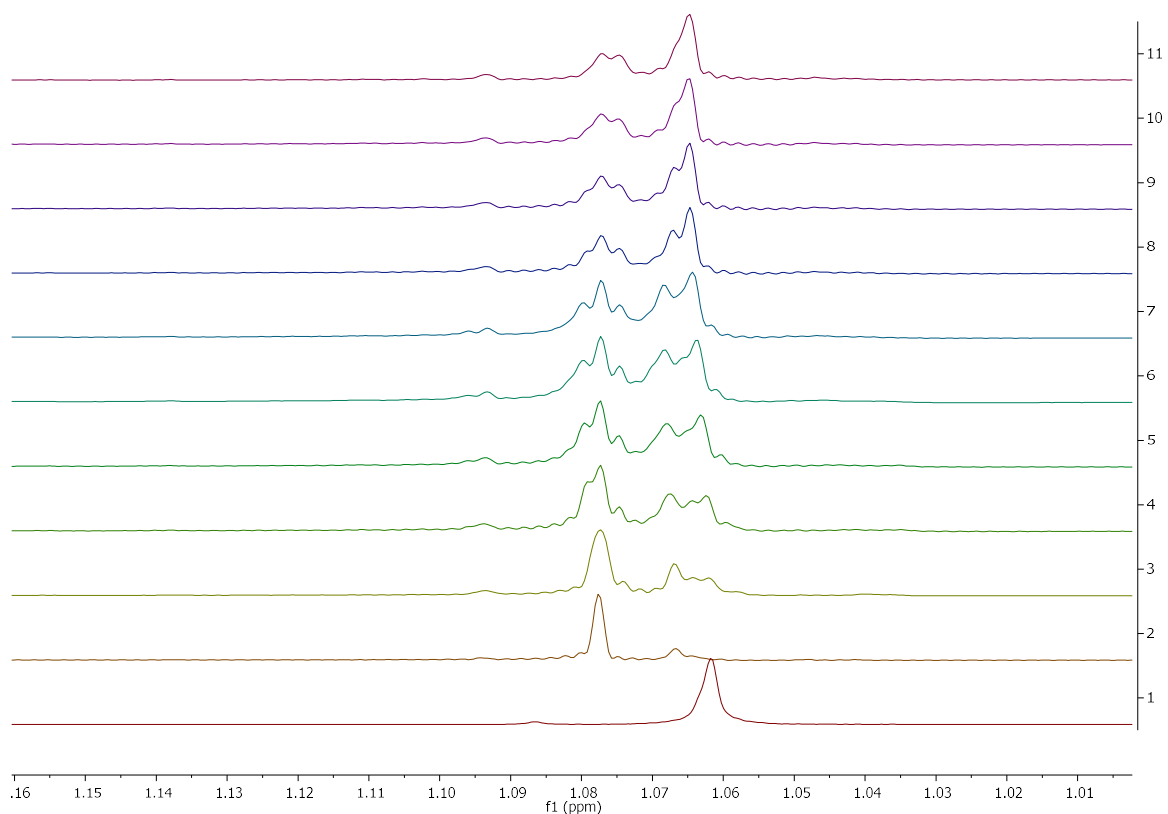
Procedure for ^1H NMR follow-up of the borylation reaction: $[\text{Ir}(\text{COD})(\text{Cl})]_2$ (2 mg, 3.0×10^{-6} mol, 0.5 eq.), B_2pin_2 (4.63 mg, 1.83×10^{-5} mol, 3 eq.), and ligand **L** (5 mg, 6.1×10^{-6} mol, 1 eq) were introduced in an oven dried NMR tube. Deuterated toluene (1 mL) and 3-methylpyridine (0.6 μL , 6.1×10^{-6} mol, 1 eq.) were added inside the NMR tube under argon atmosphere. The reaction mixture was analyzed every five minutes for 24 hours by ^1H NMR at 80°C. GC-MS analysis of the resulting mixture showed full conversion of the starting material towards the *meta*-C-H bond borylated product. The below-presented NMR spectra from top to bottom: r.t., then 80°C then every 2.4 hours at 80°C:



From the above-presented NMR spectra, there is a clear formation of H_2 (ca. 4.5 ppm) and a chemical shift in the proton singlet belonging to the COD ligand from a broad singlet (ca. 4 ppm) to an up-field shifted 3.35 ppm (as seen it is seen above in the formation of $L:(Bpin)_3$ species)

The below presented NMR spectra for the aromatic area shows the disappearance of the protons belonging to the bound substrate and emergence of new proton signals belonging to the bound product. Qualitatively, the proton peaks from the product are less up-field shifted, thus less coordinating to the zinc(II) center when compared to the substrate. This likely indicates that the substrate is more coordinating to the recognition site than the borolated product. We ascribe this difference to the high bulkiness encountered in the product with respect to the substrate.

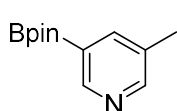




The above-presented NMR spectra for the aliphatic area shows the fast disappearance of B_2pin_2 into the catalytically active species. However, due to overlapping, it is not clear to differentiate which proton signals correspond to the catalytically active species or the potential intermediates or the borylated product.

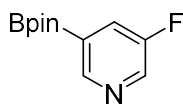
7. Characterization of products resulting from the catalytic experiments.

General procedure A: [Ir(COD)(Cl)]₂ (1.7 mg, 2.4 × 10⁻⁶ mol, 0.015 eq.), B₂pin₂ (41.1 mg, 1.62 × 10⁻⁴ mol, 1 eq.), ligand **L** (4.1 mg, 4.9 × 10⁻⁶ mol, 0.03 eq.), and dodecane (6.9 mg, 9.2 μL, 4.05 × 10⁻⁵ mol, 0.25 eq.) were introduced in an oven dried Schlenk flask. *p*-xylene (1 mL) was added and the reaction mixture was stirred at room temperature for 30 minutes. Then, the substrate (1.62 × 10⁻⁴ mol, 1 eq.) was added. Upon completion monitored by GC-MS analysis, conversion and yield were estimated using *n*-dodecane as the internal standard. The solvent was then evaporated and the residue was purified using Kugelrohr distillation apparatus yielding the analytically pure product.



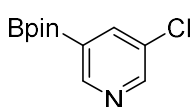
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylpyridine (5a):

Following the general procedure **A**, the reaction mixture was stirred at 80°C for 9 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (31 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.72 (s, 1H), 8.47 (s, 1H), 7.87 (s, 1H), 2.32 (s, 3H), 1.35 (s, 12H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 152.55, 152.40, 142.68, 132.29, 84.16, 24.86, 18.30 ppm. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 31.06 (s) ppm. GC: t_R = 16.5 min; MS (EI): *m/z* = 219 (M⁺, 25), 204 (50), 162 (25), 120 (100). HRMS (ESI): *m/z* calcd for (C₁₂H₁₉NO₂¹¹B) [M+H]⁺ 220.15033; found: 220.1503 (0 ppm).



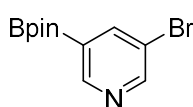
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-Fluoropyridine (5b):

Following the general procedure **A**, the reaction mixture was stirred at 80°C for 20 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (33 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.74 (s, 1H), 8.52 (s, 1H), 7.74 (dd, *J* = 8.6, 2.2 Hz, 1H), 1.35 (s, 12H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 151.12 (d, *J* = 5.1 Hz), 140.40 (d, *J* = 23.7 Hz), 128.18 (d, *J* = 16.3 Hz), 84.58, 24.84 ppm. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 30.27 (s) ppm. ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ = -127.44 (s) ppm. GC: t_R = 13.9 min; MS (EI): *m/z* = 223 (M⁺, 30), 208 (100), 166 (50), 137 (40), 124 (85), 58 (45). HRMS (ESI): *m/z* calcd for (C₁₁H₁₆NO₂F¹¹B) [M+H]⁺ 224.12526; 224.1254 (1 ppm).



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-chloropyridine (5c):

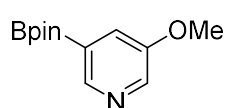
Following the general procedure **A**, the reaction mixture was stirred at 80°C for 24 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (32 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.79 (d, *J* = 1.0 Hz, 1H), 8.62 (d, *J* = 2.5 Hz, 1H), 8.03 (t, *J* = 2.5, 1.0 Hz, 1H), 1.35 (s, 12H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 152.92, 150.84, 141.66, 132.03, 84.61, 24.84 ppm. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 30.64 (s) ppm. GC: t_R = 16.4 min; MS (EI): *m/z* = 239 (M⁺, 45), 226 (35), 224 (100), 182 (45), 153 (50), 140 (80), 139 (20), 85 (30), 58 (50). HRMS (ESI): *m/z* calcd for (C₁₁H₁₆NO₂³⁵Cl¹¹B) [M+H]⁺ 240.09571; 240.0957 (0 ppm).



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-bromopyridine (5d):

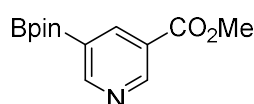
Following the general procedure **A**, the reaction mixture was stirred at 80°C for 24 hours. 91% conversion and a yield of 80% were estimated by GC-MS

analysis. Purification by Kugelrohr distillation afforded the analytically pure product (34 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.83 (d, J = 1.2 Hz, 1H), 8.72 (d, J = 2.4 Hz, 1H), 8.18 (dd, J = 2.4, 1.2 Hz, 1H), 1.35 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 153.24, 152.98, 144.53, 120.95, 84.62, 24.85 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ = 30.70 (s) ppm. GC: t_{R} = 17.7 min; MS (EI): m/z = 283 (M^+ , 30), 285 (30), 270 (95), 268 (100), 226 (30), 186 (50), 184 (50), 85 (30), 58 (70). The spectral data match those found in literature.^[12]



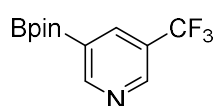
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methoxypyridine (5e):

Following the general procedure **A**, the reaction mixture was stirred at 80°C for 24 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (36 mg, 95 % yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.53 (d, J = 1.5 Hz, 1H), 8.35 (d, J = 3.1 Hz, 1H), 7.53 (t, J = 3.1, 1.5 Hz, 1H), 3.85 (s, 3H), 1.34 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 155.23, 147.54, 140.58, 125.20, 84.25, 55.47, 24.83 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ = 30.78 (s) ppm. GC: t_{R} = 17.9 min; MS (EI): m/z = 235 (M^+ , 80), 220 (50), 178 (30), 149 (80), 135 (100). The spectral data match those found in literature.^[13]



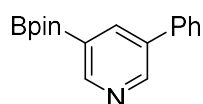
3-Pyridinecarboxylic acid, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-, methyl ester (5f):

Following the general procedure **A**, the reaction mixture was stirred at 80°C for 18 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (40 mg, 94% yield). ^1H NMR (400 MHz, CDCl_3): δ = 9.27 (d, J = 2.3 Hz, 1H), 9.08 (d, J = 1.6 Hz, 1H), 8.67 (dd, J = 2.3, 1.6 Hz, 1H), 3.95 (s, 3H), 1.37 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 165.78, 158.75, 152.84, 143.34, 125.44, 84.60, 52.36, 24.86 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ = 31.07 (s) ppm. GC: t_{R} = 19.6 min; MS (EI): m/z = 263 (M^+ , 10), 248 (35), 220 (100), 164 (85). The spectral data match those found in literature.^[14]



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylpyridine (5g):

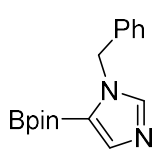
Following the general procedure **A**, the reaction mixture was stirred at 80°C for 20 hours. 50% conversion and a yield of 45 % were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the product containing traces of B_2pin_2 impurities. ^1H NMR (400 MHz, CDCl_3): δ = 9.13 (s, 1H), 8.96 (d, J = 1.7 Hz, 1H), 8.32 (s, 1H), 1.39 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ = 158.24, 148.53 (q, J = 4.2 Hz), 139.27 (q, J = 3.8 Hz), 84.81, 25.02. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ = 30.56 (s) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ = -62.64 (s) ppm. GC: t_{R} = 13.4 min; MS (EI): m/z = 273 (M^+ , 10), 258 (100), 216 (40), 174 (25), 58 (35). The spectral data match those found in literature.^[15]



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-phenylpyridine (5h):

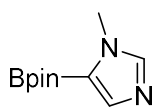
Following the general procedure **A**, the reaction mixture was stirred at 80°C for 17 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (41 mg, 89% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.92 (d, J = 1.6 Hz, 1H), 8.91 (d, J = 2.5 Hz, 1H), 8.27 (m, 1H), 7.64-7.58 (m, 2H), 7.51-7.44 (m, 2H), 7.42-7.35 (m, 1H), 1.37 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 154.07, 150.41, 140.62, 137.82, 135.87, 128.98, 128.01, 127.20,

84.32, 24.89 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): $\delta = 30.94$ (s) ppm. GC: $t_{\text{R}} = 23.4$ min; MS (EI): $m/z = 281$ (M^+ , 100), 266 (65), 224 (35), 195 (50), 181 (80). HRMS (ESI): m/z calcd for ($\text{C}_{17}\text{H}_{21}\text{NO}_2^{11}\text{B}$) [$\text{M}+\text{H}$] $^+$ 282.16598; 282.1664 (2 ppm).



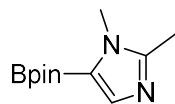
1-Benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (6a):

Following the general procedure **A**, the reaction mixture was stirred at 80°C for 24 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (44 mg, 95% yield.). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.65$ (d, $J = 11.6$ Hz, 2H), 7.36-7.24 (m, 3H), 7.14 (d, $J = 6.7$ Hz, 2H), 5.37 (s, 2H), 1.25 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 142.21$, 141.72, 137.62, 128.58, 127.67, 127.11, 83.71, 50.46, 24.63 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): $\delta = 28.01$ (s) ppm. GC: $t_{\text{R}} = 22.7$ min; MS (EI): $m/z = 284$ (M^+ , 40), 184 (95), 168 (20), 91 (100). The spectral data match those found in literature.^[16]



1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (6b):

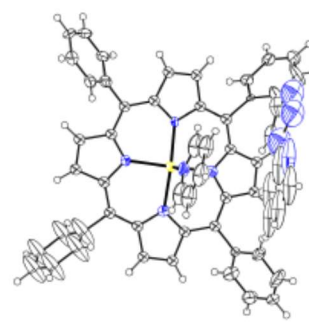
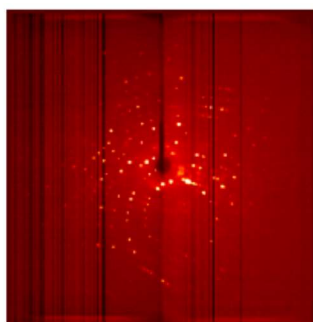
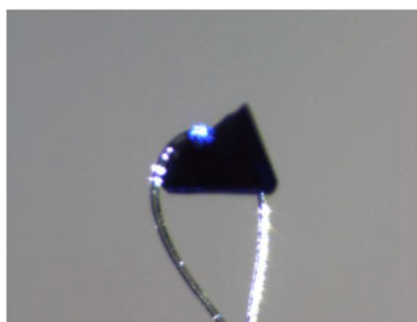
Following the general procedure **A**, the reaction mixture was stirred at 80°C for 24 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (30 mg, 90% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.56$ (s, 1H), 7.54 (s, 1H), 3.79 (s, 3H), 1.31 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 141.98$, 141.50, 83.62, 33.96, 24.80 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): $\delta = 28.59$ (s) ppm. GC: $t_{\text{R}} = 16.6$ min; MS (EI): $m/z = 208$ (M^+ , 60), 193 (25), 165 (40), 123 (30), 108 (100), 83 (25), 81 (25). The spectral data match those found in literature.^[16]



1,2-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (6c):

Following the general procedure **A**, the reaction mixture was stirred at 80°C for 24 hours. Quantitative conversion and yield were estimated by GC-MS analysis. Purification by Kugelrohr distillation afforded the analytically pure product (35 mg, 97% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.41$ (s, 1H), 3.66 (s, 3H), 2.35 (s, 3H), 1.27 (s, 12H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 149.52$, 140.27, 83.39, 32.59, 24.73, 13.11 ppm. $^{11}\text{B}\{^1\text{H}\}$ (128 MHz, CDCl_3): $\delta = 28.06$ (s) ppm. GC: $t_{\text{R}} = 17.5$ min; MS (EI): $m/z = 222$ (M^+ , 95), 122 (100), 179 (50), 137 (35), 56 (20), 81 (15), 207 (15). The spectral data match those found in literature.^[16]

8. X-ray crystallographic data of [L:pyridine] CCDC-2061921.



($C_{56}H_{37}N_9Zn$); $M = 901.31$. A suitable crystal for X-ray diffraction single crystal experiment (violet prism, dimensions = 0.420 x 0.260 x 0.090 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector,^[*] using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator) at $T = 150(2) \text{ K}$. Crystal structure has been described in triclinic symmetry and P1 (I.T.#2) centric space group. Cell parameters have been refined as follows: $a = 14.501(3)$, $b = 14.535(3)$, $c = 14.498(3) \text{ \AA}$, $\alpha = 109.035(6)$, $\beta = 117.797(6)$, $\gamma = 93.180(7)^\circ$, $V = 2475.3(8) \text{ \AA}^3$. Number of formula unit Z is equal to 2 and calculated density d and absorption coefficient μ values are 1.209 g.cm^{-3} and 0.542 mm^{-1} respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,^[17] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program).^[18] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,^[19] implemented as the *SQUEEZE* option in *PLATON*.^[20] A new data set, free of solvent contribution, was then used in the final refinement. All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 10937 unique intensities and 374 parameters converged at $\omega R(F^2) = 0.2862$ ($R_F = 0.1118$) for 9539 observed reflections with ($I > 2\sigma$).

[*] Thanks to FEDER funds.

8.1. Data data collection strategy details.

Software: BIS V6.2.1/2016-03-01
Number of scans: 4
Total number of frames [*]: 1104
Total length of scans [*]: 552.00 (deg.)
Rotation speed [*]: 80.00 sec./deg.
Total exposition time [*]: 12 h 16.0 min.

[*] fast scan not included

Measurement mode: shutterless mode

Scan	Time(s)	Width	DX (mm)	Frames	Theta	Omega	Phi	Chi	T(K)
1 Phi	40.0	0.50	34.0	720	0.27	270.94	360.00	23.00	150.00
2 Omega	40.0	0.50	34.0	192	0.27	3.16	0.00	315.50	150.00
3 Omega	40.0	0.50	34.0	192	0.27	3.16	144.00	315.50	150.00
2 Fast	8.0	1.00	34.0	180	0.00	360.00	0.00	54.74	150.01

8.2. Structural data.

... Crystal data ...

Empirical formula	C ₅₆ H ₃₇ N ₉ Zn
Formula weight	901.31 g/mol
Temperature	150(2) K
Radiation type	Mo-K α
Wavelength	0.71073 Å
Crystal system, space group	triclinic, <i>P</i> 1
Unit cell dimensions	$a = 14.501(3)$ Å $b = 14.535(3)$ Å $c = 14.498(3)$ Å $\alpha = 109.035(5)$ ° $\beta = 117.797(6)$ ° $\gamma = 93.180(7)$ °
Volume	2475.3(8) Å ³
Z, Calculated density	2, 1.209 g.cm ⁻³
Absorption coefficient	0.542 mm ⁻¹
F(000)	932
Crystal size	0.420 x 0.260 x 0.090 mm
Crystal color	violet
Crystal description	prism

... Data collection ...

Diffractometer	D8 Venture diffractometer
Θ range for data collection	2.445 to 27.507 °
$(\sin \Theta / \lambda)_{\max}$ (Å ⁻¹)	0.650
h_{\min}, h_{\max}	-18, 16
k_{\min}, k_{\max}	-18, 17
l_{\min}, l_{\max}	0, 18
Reflections collected / unique	10937 / 10937 [R(int) = ?]
Reflections [$I > 2\sigma$]	9539
Completeness to Θ_{\max}	0.958
Absorption correction type	multi-scan
Max. and min. transmission	0.952 , 0.674

... Refinement ...

Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	10937 / 0 / 374
Goodness-of-fit	1.030
Final R indices [$I > 2\sigma$]	$R_1 = 0.1118$, $\omega R_2 = 0.2862$
R indices (all data)	$R_1 = 0.1287$, $\omega R_2 = 0.3055$
$\Delta\rho_{\max}, \Delta\rho_{\min}$	1.604, -1.781 e.Å ⁻³

8.3. Fractional atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (\AA^2).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	U(eq)	adp
Zn1	0.18822(7)	0.54801(6)	0.33485(8)	1	0.0261(2)	Uani
N1	0.1590(5)	0.6775(5)	0.3084(5)	1	0.0288(13)	Uani
N2	0.1642(5)	0.4845(5)	0.1733(5)	1	0.0333(14)	Uani
N3	0.1573(5)	0.4056(4)	0.3306(5)	1	0.0279(12)	Uani
N4	0.1628(5)	0.6008(4)	0.4692(5)	1	0.0255(12)	Uani
C1	0.1555(7)	0.6994(6)	0.2215(7)	1	0.0351(4)	Uani
C2	0.1733(8)	0.6390(5)	0.1359(7)	1	0.0351(4)	Uani
C3	0.1744(7)	0.5352(5)	0.1139(7)	1	0.0351(4)	Uani
C4	0.1808(8)	0.4692(5)	0.0196(7)	1	0.0351(4)	Uani
H4	0.190825	0.486855	-0.033224	1	0.042	Uiso
C5	0.1698(7)	0.3772(6)	0.0215(7)	1	0.0351(4)	Uani
H5	0.167752	0.317144	-0.032321	1	0.042	Uiso
C6	0.1617(7)	0.3854(6)	0.1183(7)	1	0.0351(4)	Uani
C7	0.1478(7)	0.3068(6)	0.1493(7)	1	0.0351(4)	Uani
C8	0.1421(7)	0.3155(6)	0.2470(7)	1	0.0351(4)	Uani
C9	0.1245(7)	0.2327(6)	0.2744(7)	1	0.0351(4)	Uani
H9	0.113309	0.163674	0.231171	1	0.042	Uiso
C10	0.1271(7)	0.2728(6)	0.3750(7)	1	0.0351(4)	Uani
H10	0.115410	0.236475	0.414093	1	0.042	Uiso
C11	0.1509(7)	0.3813(6)	0.4112(7)	1	0.0351(4)	Uani
C12	0.1672(7)	0.4500(5)	0.5146(7)	1	0.0351(4)	Uani
C13	0.1757(8)	0.5528(5)	0.5429(7)	1	0.0351(4)	Uani
C14	0.1853(8)	0.6246(5)	0.6448(7)	1	0.0351(4)	Uani
H14	0.196647	0.612127	0.709194	1	0.042	Uiso
C15	0.1755(8)	0.7132(6)	0.6331(7)	1	0.0351(4)	Uani
H15	0.175716	0.772949	0.685776	1	0.042	Uiso
C16	0.1645(7)	0.6984(6)	0.5242(7)	1	0.0351(4)	Uani
C17	0.1516(7)	0.7713(6)	0.4785(7)	1	0.0351(4)	Uani
C18	0.1439(7)	0.7586(6)	0.3755(7)	1	0.0351(4)	Uani
C19	0.1268(7)	0.8327(6)	0.3264(7)	1	0.0351(4)	Uani
H19	0.110594	0.894708	0.353924	1	0.042	Uiso
C20	0.1381(7)	0.7980(6)	0.2340(7)	1	0.0351(4)	Uani
H20	0.135135	0.832110	0.187131	1	0.042	Uiso
C21	0.1871(8)	0.6825(5)	0.0618(7)	1	0.0341(16)	Uani
C22	0.2763(12)	0.7589(8)	0.1104(9)	1	0.074(4)	Uani
H22	0.326293	0.784818	0.189852	1	0.089	Uiso
C23	0.2929(14)	0.7984(10)	0.0411(11)	1	0.094(6)	Uani
H23	0.356571	0.848178	0.072262	1	0.113	Uiso

C24	0.2156(15)	0.7639(8)	-0.0726(10)	1	0.080(5)	Uani
H24	0.224848	0.793483	-0.118279	1	0.096	Uiso
C25	0.1265(9)	0.6889(8)	-0.1215(9)	1	0.048(2)	Uani
H25	0.074797	0.665160	-0.200312	1	0.058	Uiso
C26	0.1128(8)	0.6479(8)	-0.0537(8)	1	0.045(2)	Uani
H26	0.051154	0.595035	-0.086935	1	0.054	Uiso
C31	0.1324(9)	0.2006(6)	0.0734(11)	1	0.129(3)	Uani
C32	0.0310(8)	0.1345(8)	0.0041(12)	1	0.129(3)	Uani
H32	-0.029157	0.155364	0.006260	1	0.155	Uiso
C33	0.0176(8)	0.0379(7)	-0.0685(11)	1	0.129(3)	Uani
H33	-0.051779	-0.007341	-0.115835	1	0.155	Uiso
C34	0.1056(9)	0.0073(6)	-0.0717(11)	1	0.129(3)	Uani
H34	0.096376	-0.058711	-0.121226	1	0.155	Uiso
C35	0.2070(8)	0.0735(8)	-0.0023(11)	1	0.129(3)	Uani
H35	0.267155	0.052623	-0.004522	1	0.155	Uiso
C36	0.2204(8)	0.1701(7)	0.0702(11)	1	0.129(3)	Uani
H36	0.289779	0.215329	0.117575	1	0.155	Uiso
C41	0.1754(6)	0.4105(5)	0.5990(6)	1	0.0313(15)	Uani
C42	0.2532(6)	0.3614(6)	0.6419(7)	1	0.0354(16)	Uani
H42	0.303071	0.353041	0.616526	1	0.042	Uiso
C43	0.2612(8)	0.3231(6)	0.7226(8)	1	0.0438(19)	Uani
H43	0.315520	0.289121	0.750288	1	0.053	Uiso
C44	0.1907(11)	0.3350(6)	0.7608(8)	1	0.053(2)	Uani
H44	0.195928	0.310227	0.815678	1	0.063	Uiso
C45	0.1105(9)	0.3845(7)	0.7178(8)	1	0.047(2)	Uani
H45	0.060677	0.392110	0.743365	1	0.056	Uiso
C46	0.1024(7)	0.4220(6)	0.6396(7)	1	0.0341(16)	Uani
H46	0.047839	0.455920	0.612450	1	0.041	Uiso
C51	0.1419(7)	0.8701(5)	0.5463(6)	1	0.0315(16)	Uani
C52	0.0510(11)	0.8728(7)	0.5522(10)	1	0.058(3)	Uani
H52	-0.005788	0.813637	0.511609	1	0.070	Uiso
C53	0.0408(13)	0.9618(8)	0.6173(12)	1	0.076(4)	Uani
H53	-0.022794	0.964037	0.621139	1	0.092	Uiso
C54	0.1250(15)	1.0472(8)	0.6766(13)	1	0.086(5)	Uani
H54	0.117848	1.108675	0.719443	1	0.103	Uiso
C55	0.2155(14)	1.0444(8)	0.6744(13)	1	0.094(5)	Uani
H55	0.272293	1.103757	0.717578	1	0.112	Uiso
C56	0.2300(9)	0.9563(7)	0.6100(10)	1	0.058(3)	Uani
C57	0.3332(16)	0.9532(10)	0.6327(14)	1	0.094(5)	Uani
N58	0.4259(13)	1.0145(14)	0.7327(14)	1	0.125(4)	Uani
N59	0.5126(13)	0.9994(13)	0.7176(15)	1	0.125(4)	Uani
N60	0.4831(14)	0.9306(13)	0.6044(15)	1	0.125(4)	Uani
C61	0.3692(12)	0.9072(9)	0.5565(13)	1	0.075(3)	Uani
H61	0.320735	0.863946	0.479155	1	0.091	Uiso

C62	0.5472(14)	0.9100(13)	0.563(2)	1	0.147(5)	Uani
N63	0.6598(12)	0.9487(10)	0.6558(19)	1	0.147(5)	Uani
C64	0.7223(13)	0.9280(14)	0.600(2)	1	0.147(5)	Uani
H64	0.797180	0.958923	0.642975	1	0.177	Uiso
C65	0.6785(14)	0.8685(13)	0.494(2)	1	0.147(5)	Uani
H65	0.728333	0.843366	0.473698	1	0.177	Uiso
C66	0.5640(14)	0.8319(13)	0.398(2)	1	0.147(5)	Uani
H66	0.537863	0.800959	0.318559	1	0.177	Uiso
C67	0.5057(15)	0.8536(13)	0.451(2)	1	0.147(5)	Uani
H67	0.429949	0.826637	0.405812	1	0.177	Uiso
N71	0.3600(5)	0.5904(5)	0.4274(7)	1	0.0388(14)	Uani
C72	0.4132(9)	0.6518(9)	0.5388(13)	1	0.0694(14)	Uani
H72	0.373940	0.673164	0.575692	1	0.083	Uiso
C73	0.5276(9)	0.6849(9)	0.6016(13)	1	0.0694(14)	Uani
H73	0.566327	0.731632	0.678716	1	0.083	Uiso
C74	0.5807(8)	0.6433(10)	0.5411(13)	1	0.0694(14)	Uani
H74	0.657106	0.658973	0.580185	1	0.083	Uiso
C75	0.5267(9)	0.5853(9)	0.4355(13)	1	0.0694(14)	Uani
H75	0.562612	0.560766	0.395452	1	0.083	Uiso
C76	0.4178(9)	0.5593(9)	0.3810(13)	1	0.0694(14)	Uani
H76	0.380141	0.514929	0.302972	1	0.083	Uiso

8.4. Anisotropic displacement parameters (\AA^2).

The anisotropic displacement factor exponent takes the form: $-2\pi[h^2a^{*2}U_{11}+\dots +2hka^*b^*U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
Zn1	0.0363(4)	0.0206(3)	0.0293(4)	0.0083(3)	0.0237(4)	0.0084(4)
N1	0.036(3)	0.026(3)	0.030(3)	0.009(2)	0.021(3)	0.009(2)
N2	0.044(4)	0.030(3)	0.028(3)	0.011(3)	0.021(3)	0.005(3)
N3	0.037(3)	0.019(3)	0.031(3)	0.007(2)	0.022(3)	0.004(2)
N4	0.041(3)	0.012(2)	0.031(3)	0.007(2)	0.025(3)	0.005(2)
C1	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C2	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C3	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C4	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C5	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C6	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C7	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C8	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C9	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C10	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C11	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C12	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)

C13	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C14	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C15	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C16	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C17	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C18	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C19	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C20	0.0579(10)	0.0240(8)	0.0346(9)	0.0115(7)	0.0320(9)	0.0128(8)
C21	0.071(5)	0.020(3)	0.031(4)	0.015(3)	0.037(4)	0.017(4)
C22	0.127(11)	0.042(5)	0.030(5)	0.001(4)	0.037(6)	-0.033(6)
C23	0.139(13)	0.061(7)	0.060(7)	0.021(6)	0.043(8)	-0.041(8)
C24	0.181(16)	0.034(5)	0.063(7)	0.022(5)	0.090(10)	0.020(7)
C25	0.068(6)	0.048(5)	0.047(5)	0.025(4)	0.038(5)	0.025(5)
C26	0.040(4)	0.056(6)	0.041(5)	0.022(4)	0.021(4)	0.009(4)
C31	0.118(6)	0.060(4)	0.131(6)	-0.032(4)	0.053(5)	0.018(4)
C32	0.118(6)	0.060(4)	0.131(6)	-0.032(4)	0.053(5)	0.018(4)
C33	0.118(6)	0.060(4)	0.131(6)	-0.032(4)	0.053(5)	0.018(4)
C34	0.118(6)	0.060(4)	0.131(6)	-0.032(4)	0.053(5)	0.018(4)
C35	0.118(6)	0.060(4)	0.131(6)	-0.032(4)	0.053(5)	0.018(4)
C36	0.118(6)	0.060(4)	0.131(6)	-0.032(4)	0.053(5)	0.018(4)
C41	0.029(4)	0.028(3)	0.028(4)	0.004(3)	0.014(3)	-0.001(3)
C42	0.040(4)	0.026(3)	0.039(4)	0.008(3)	0.022(3)	0.005(3)
C43	0.063(5)	0.029(4)	0.045(5)	0.015(4)	0.031(4)	0.013(4)
C44	0.100(7)	0.036(4)	0.037(5)	0.014(4)	0.048(5)	0.002(5)
C45	0.068(6)	0.041(5)	0.034(4)	0.002(4)	0.038(5)	-0.003(4)
C46	0.041(4)	0.031(4)	0.030(4)	0.005(3)	0.023(3)	0.004(3)
C51	0.075(5)	0.017(3)	0.029(3)	0.016(3)	0.041(4)	0.019(3)
C52	0.111(9)	0.035(5)	0.083(7)	0.028(5)	0.086(7)	0.034(5)
C53	0.164(13)	0.042(5)	0.118(10)	0.045(6)	0.131(11)	0.055(7)
C54	0.180(15)	0.036(5)	0.106(10)	0.030(6)	0.119(11)	0.044(7)
C55	0.122(13)	0.029(5)	0.098(10)	-0.015(6)	0.061(10)	0.012(6)
C56	0.063(6)	0.026(4)	0.077(7)	0.001(4)	0.043(6)	0.006(4)
C57	0.130(13)	0.047(7)	0.098(11)	0.010(7)	0.068(11)	-0.011(8)
N58	0.092(6)	0.120(8)	0.104(6)	0.035(6)	0.016(6)	-0.019(6)
N59	0.092(6)	0.120(8)	0.104(6)	0.035(6)	0.016(6)	-0.019(6)
N60	0.092(6)	0.120(8)	0.104(6)	0.035(6)	0.016(6)	-0.019(6)
C61	0.089(9)	0.046(6)	0.095(10)	0.035(6)	0.046(8)	0.017(6)
C62	0.068(4)	0.067(4)	0.249(12)	0.089(6)	0.023(5)	-0.002(3)
N63	0.068(4)	0.067(4)	0.249(12)	0.089(6)	0.023(5)	-0.002(3)
C64	0.068(4)	0.067(4)	0.249(12)	0.089(6)	0.023(5)	-0.002(3)
C65	0.068(4)	0.067(4)	0.249(12)	0.089(6)	0.023(5)	-0.002(3)
C66	0.068(4)	0.067(4)	0.249(12)	0.089(6)	0.023(5)	-0.002(3)
C67	0.068(4)	0.067(4)	0.249(12)	0.089(6)	0.023(5)	-0.002(3)
N71	0.041(3)	0.025(3)	0.062(5)	0.016(3)	0.037(4)	0.007(3)

C72	0.041(2)	0.063(3)	0.116(5)	0.047(3)	0.041(3)	0.012(2)
C73	0.041(2)	0.063(3)	0.116(5)	0.047(3)	0.041(3)	0.012(2)
C74	0.041(2)	0.063(3)	0.116(5)	0.047(3)	0.041(3)	0.012(2)
C75	0.041(2)	0.063(3)	0.116(5)	0.047(3)	0.041(3)	0.012(2)
C76	0.041(2)	0.063(3)	0.116(5)	0.047(3)	0.041(3)	0.012(2)

8.5. Bond length [Å].

Zn1 - N4 = 2.061(5)
 Zn1 - N2 = 2.062(6)
 Zn1 - N1 = 2.068(6)
 Zn1 - N3 = 2.068(6)
 Zn1 - N71 = 2.135(6)
 N1 - C18 = 1.365(9)
 N1 - C1 = 1.377(9)
 N2 - C3 = 1.352(9)
 N2 - C6 = 1.388(10)
 N3 - C11 = 1.366(9)
 N3 - C8 = 1.385(9)
 N4 - C16 = 1.374(9)
 N4 - C13 = 1.407(9)
 C1 - C2 = 1.411(10)
 C1 - C20 = 1.437(10)
 C2 - C3 = 1.439(10)
 C2 - C21 = 1.491(9)
 C3 - C4 = 1.439(9)
 C4 - C5 = 1.349(10)
 C4 - H4 = 0.9500
 C5 - C6 = 1.429(10)
 C5 - H5 = 0.9500
 C6 - C7 = 1.394(10)
 C7 - C8 = 1.421(10)
 C7 - C31 = 1.506(9)
 C8 - C9 = 1.429(10)
 C9 - C10 = 1.365(10)
 C9 - H9 = 0.9500
 C10 - C11 = 1.454(10)
 C10 - H10 = 0.9500
 C11 - C12 = 1.403(10)
 C12 - C13 = 1.396(10)
 C12 - C41 = 1.473(10)
 C13 - C14 = 1.441(9)
 C14 - C15 = 1.360(10)
 C14 - H14 = 0.9500
 C15 - C16 = 1.450(10)

C15 - H15 = 0.9500
C16 - C17 = 1.400(10)
C17 - C18 = 1.392(10)
C17 - C51 = 1.510(9)
C18 - C19 = 1.447(10)
C19 - C20 = 1.360(10)
C19 - H19 = 0.9500
C20 - H20 = 0.9500
C21 - C22 = 1.372(14)
C21 - C26 = 1.388(13)
C22 - C23 = 1.409(13)
C22 - H22 = 0.9500
C23 - C24 = 1.379(19)
C23 - H23 = 0.9500
C24 - C25 = 1.359(18)
C24 - H24 = 0.9500
C25 - C26 = 1.381(13)
C25 - H25 = 0.9500
C26 - H26 = 0.9500
C31 - C32 = 1.3900
C31 - C36 = 1.3900
C32 - C33 = 1.3900
C32 - H32 = 0.9500
C33 - C34 = 1.3900
C33 - H33 = 0.9500
C34 - C35 = 1.3900
C34 - H34 = 0.9500
C35 - C36 = 1.3900
C35 - H35 = 0.9500
C36 - H36 = 0.9500
C41 - C42 = 1.376(11)
C41 - C46 = 1.426(10)
C42 - C43 = 1.414(12)
C42 - H42 = 0.9500
C43 - C44 = 1.366(14)
C43 - H43 = 0.9500
C44 - C45 = 1.402(16)
C44 - H44 = 0.9500
C45 - C46 = 1.373(12)
C45 - H45 = 0.9500
C46 - H46 = 0.9500
C51 - C52 = 1.362(13)
C51 - C56 = 1.422(12)
C52 - C53 = 1.395(11)

C52 - H52 = 0.9500
C53 - C54 = 1.39(2)
C53 - H53 = 0.9500
C54 - C55 = 1.33(2)
C54 - H54 = 0.9500
C55 - C56 = 1.410(13)
C55 - H55 = 0.9500
C56 - C57 = 1.38(2)
C57 - N58 = 1.38(2)
C57 - C61 = 1.43(2)
N58 - N59 = 1.39(3)
N59 - N60 = 1.45(2)
N60 - C62 = 1.33(3)
N60 - C61 = 1.43(2)
C61 - H61 = 0.9500
C62 - C67 = 1.35(4)
C62 - N63 = 1.47(2)
N63 - C64 = 1.45(3)
C64 - C65 = 1.30(4)
C64 - H64 = 0.9500
C65 - C66 = 1.50(3)
C65 - H65 = 0.9500
C66 - C67 = 1.38(4)
C66 - H66 = 0.9500
C67 - H67 = 0.9500
N71 - C76 = 1.315(14)
N71 - C72 = 1.349(16)
C72 - C73 = 1.424(15)
C72 - H72 = 0.9500
C73 - C74 = 1.437(18)
C73 - H73 = 0.9500
C74 - C75 = 1.279(19)
C74 - H74 = 0.9500
C75 - C76 = 1.355(15)
C75 - H75 = 0.9500
C76 - H76 = 0.9500

8.6. Angles [°].

N4 - Zn1 - N2 = 162.9(2)
N4 - Zn1 - N1 = 88.3(2)
N2 - Zn1 - N1 = 88.4(2)
N4 - Zn1 - N3 = 87.8(2)
N2 - Zn1 - N3 = 89.3(2)
N1 - Zn1 - N3 = 159.2(2)

N4 - Zn1 - N71 = 99.0(3)
N2 - Zn1 - N71 = 98.2(3)
N1 - Zn1 - N71 = 99.0(3)
N3 - Zn1 - N71 = 101.8(3)
C18 - N1 - C1 = 107.1(6)
C18 - N1 - Zn1 = 126.8(5)
C1 - N1 - Zn1 = 126.0(5)
C3 - N2 - C6 = 106.7(6)
C3 - N2 - Zn1 = 125.8(5)
C6 - N2 - Zn1 = 125.8(5)
C11 - N3 - C8 = 105.9(6)
C11 - N3 - Zn1 = 127.1(5)
C8 - N3 - Zn1 = 127.0(5)
C16 - N4 - C13 = 106.3(6)
C16 - N4 - Zn1 = 126.2(5)
C13 - N4 - Zn1 = 124.6(4)
N1 - C1 - C2 = 126.4(7)
N1 - C1 - C20 = 110.0(6)
C2 - C1 - C20 = 123.4(7)
C1 - C2 - C3 = 122.6(7)
C1 - C2 - C21 = 119.1(6)
C3 - C2 - C21 = 118.3(6)
N2 - C3 - C2 = 126.0(6)
N2 - C3 - C4 = 110.4(6)
C2 - C3 - C4 = 123.6(6)
C5 - C4 - C3 = 106.1(6)
C5 - C4 - H4 = 126.9
C3 - C4 - H4 = 126.9
C4 - C5 - C6 = 108.3(6)
C4 - C5 - H5 = 125.9
C6 - C5 - H5 = 125.9
N2 - C6 - C7 = 125.4(7)
N2 - C6 - C5 = 108.4(6)
C7 - C6 - C5 = 126.1(7)
C6 - C7 - C8 = 126.0(7)
C6 - C7 - C31 = 119.7(9)
C8 - C7 - C31 = 114.2(9)
N3 - C8 - C7 = 124.5(7)
N3 - C8 - C9 = 111.0(6)
C7 - C8 - C9 = 124.5(7)
C10 - C9 - C8 = 106.2(7)
C10 - C9 - H9 = 126.9
C8 - C9 - H9 = 126.9
C9 - C10 - C11 = 107.2(7)

C9 - C10 - H10 = 126.4
C11 - C10 - H10 = 126.4
N3 - C11 - C12 = 125.6(7)
N3 - C11 - C10 = 109.7(6)
C12 - C11 - C10 = 124.7(7)
C13 - C12 - C11 = 124.7(7)
C13 - C12 - C41 = 117.8(6)
C11 - C12 - C41 = 117.5(6)
C12 - C13 - N4 = 124.6(6)
C12 - C13 - C14 = 126.4(7)
N4 - C13 - C14 = 108.5(6)
C15 - C14 - C13 = 108.4(6)
C15 - C14 - H14 = 125.8
C13 - C14 - H14 = 125.8
C14 - C15 - C16 = 106.4(6)
C14 - C15 - H15 = 126.8
C16 - C15 - H15 = 126.8
N4 - C16 - C17 = 124.5(7)
N4 - C16 - C15 = 110.3(6)
C17 - C16 - C15 = 125.1(7)
C18 - C17 - C16 = 125.5(7)
C18 - C17 - C51 = 118.4(6)
C16 - C17 - C51 = 116.1(6)
N1 - C18 - C17 = 125.7(7)
N1 - C18 - C19 = 108.7(6)
C17 - C18 - C19 = 125.4(7)
C20 - C19 - C18 = 107.9(7)
C20 - C19 - H19 = 126.0
C18 - C19 - H19 = 126.0
C19 - C20 - C1 = 106.1(7)
C19 - C20 - H20 = 127.0
C1 - C20 - H20 = 127.0
C22 - C21 - C26 = 119.6(7)
C22 - C21 - C2 = 118.4(8)
C26 - C21 - C2 = 122.0(8)
C21 - C22 - C23 = 119.3(10)
C21 - C22 - H22 = 120.4
C23 - C22 - H22 = 120.4
C24 - C23 - C22 = 119.1(11)
C24 - C23 - H23 = 120.5
C22 - C23 - H23 = 120.5
C25 - C24 - C23 = 122.0(9)
C25 - C24 - H24 = 119.0
C23 - C24 - H24 = 119.0

C24 - C25 - C26 = 118.4(10)
C24 - C25 - H25 = 120.8
C26 - C25 - H25 = 120.8
C25 - C26 - C21 = 121.4(9)
C25 - C26 - H26 = 119.3
C21 - C26 - H26 = 119.3
C32 - C31 - C36 = 120.0
C32 - C31 - C7 = 120.7(7)
C36 - C31 - C7 = 119.3(7)
C33 - C32 - C31 = 120.0
C33 - C32 - H32 = 120.0
C31 - C32 - H32 = 120.0
C32 - C33 - C34 = 120.0
C32 - C33 - H33 = 120.0
C34 - C33 - H33 = 120.0
C33 - C34 - C35 = 120.0
C33 - C34 - H34 = 120.0
C35 - C34 - H34 = 120.0
C36 - C35 - C34 = 120.0
C36 - C35 - H35 = 120.0
C34 - C35 - H35 = 120.0
C35 - C36 - C31 = 120.0
C35 - C36 - H36 = 120.0
C31 - C36 - H36 = 120.0
C42 - C41 - C46 = 117.3(7)
C42 - C41 - C12 = 121.8(7)
C46 - C41 - C12 = 120.9(7)
C41 - C42 - C43 = 122.1(8)
C41 - C42 - H42 = 119.0
C43 - C42 - H42 = 119.0
C44 - C43 - C42 = 119.8(9)
C44 - C43 - H43 = 120.1
C42 - C43 - H43 = 120.1
C43 - C44 - C45 = 119.0(8)
C43 - C44 - H44 = 120.5
C45 - C44 - H44 = 120.5
C46 - C45 - C44 = 121.4(8)
C46 - C45 - H45 = 119.3
C44 - C45 - H45 = 119.3
C45 - C46 - C41 = 120.4(8)
C45 - C46 - H46 = 119.8
C41 - C46 - H46 = 119.8
C52 - C51 - C56 = 121.0(7)
C52 - C51 - C17 = 118.7(8)

C56 - C51 - C17 = 120.1(8)
C51 - C52 - C53 = 120.4(11)
C51 - C52 - H52 = 119.8
C53 - C52 - H52 = 119.8
C54 - C53 - C52 = 118.9(11)
C54 - C53 - H53 = 120.5
C52 - C53 - H53 = 120.5
C55 - C54 - C53 = 121.1(10)
C55 - C54 - H54 = 119.5
C53 - C54 - H54 = 119.5
C54 - C55 - C56 = 122.2(12)
C54 - C55 - H55 = 118.9
C56 - C55 - H55 = 118.9
C57 - C56 - C55 = 118.0(12)
C57 - C56 - C51 = 123.9(9)
C55 - C56 - C51 = 116.4(10)
C56 - C57 - N58 = 124.7(16)
C56 - C57 - C61 = 129.4(15)
N58 - C57 - C61 = 104.5(17)
C57 - N58 - N59 = 107.8(17)
N58 - N59 - N60 = 114.5(15)
C62 - N60 - C61 = 134.3(19)
C62 - N60 - N59 = 127.6(18)
C61 - N60 - N59 = 97.7(16)
C57 - C61 - N60 = 115.4(16)
C57 - C61 - H61 = 122.3
N60 - C61 - H61 = 122.3
N60 - C62 - C67 = 120.5(17)
N60 - C62 - N63 = 109(3)
C67 - C62 - N63 = 130(2)
C64 - N63 - C62 = 105(2)
C65 - C64 - N63 = 121.7(16)
C65 - C64 - H64 = 119.1
N63 - C64 - H64 = 119.1
C64 - C65 - C66 = 132(3)
C64 - C65 - H65 = 114.0
C66 - C65 - H65 = 114.0
C67 - C66 - C65 = 104(3)
C67 - C66 - H66 = 128.2
C65 - C66 - H66 = 128.2
C62 - C67 - C66 = 125.4(19)
C62 - C67 - H67 = 117.3
C66 - C67 - H67 = 117.3
C76 - N71 - C72 = 117.6(8)

C76 - N71 - Zn1 = 123.0(8)
C72 - N71 - Zn1 = 119.4(6)
N71 - C72 - C73 = 120.7(12)
N71 - C72 - H72 = 119.6
C73 - C72 - H72 = 119.6
C72 - C73 - C74 = 115.8(13)
C72 - C73 - H73 = 122.1
C74 - C73 - H73 = 122.1
C75 - C74 - C73 = 121.0(10)
C75 - C74 - H74 = 119.5
C73 - C74 - H74 = 119.5
C74 - C75 - C76 = 119.5(13)
C74 - C75 - H75 = 120.3
C76 - C75 - H75 = 120.3
N71 - C76 - C75 = 125.3(14)
N71 - C76 - H76 = 117.4
C75 - C76 - H76 = 117.4

8.7. Torsion angles [°].

C18 - N1 - C1 - C2 = 176.2(9)
Zn1 - N1 - C1 - C2 = -1.4(12)
C18 - N1 - C1 - C20 = 0.3(9)
Zn1 - N1 - C1 - C20 = -177.3(6)
N1 - C1 - C2 - C3 = 14.1(14)
C20 - C1 - C2 - C3 = -170.4(9)
N1 - C1 - C2 - C21 = -168.4(8)
C20 - C1 - C2 - C21 = 7.0(14)
C6 - N2 - C3 - C2 = 175.6(9)
Zn1 - N2 - C3 - C2 = -18.9(13)
C6 - N2 - C3 - C4 = -1.2(10)
Zn1 - N2 - C3 - C4 = 164.3(6)
C1 - C2 - C3 - N2 = -3.3(15)
C21 - C2 - C3 - N2 = 179.2(9)
C1 - C2 - C3 - C4 = 173.1(9)
C21 - C2 - C3 - C4 = -4.4(14)
N2 - C3 - C4 - C5 = 2.5(10)
C2 - C3 - C4 - C5 = -174.4(9)
C3 - C4 - C5 - C6 = -2.7(10)
C3 - N2 - C6 - C7 = -177.4(9)
Zn1 - N2 - C6 - C7 = 17.1(12)
C3 - N2 - C6 - C5 = -0.5(10)
Zn1 - N2 - C6 - C5 = -166.0(6)
C4 - C5 - C6 - N2 = 2.1(10)
C4 - C5 - C6 - C7 = 179.0(9)

N2 - C6 - C7 - C8 = -5.1(15)
C5 - C6 - C7 - C8 = 178.5(9)
N2 - C6 - C7 - C31 = 172.2(9)
C5 - C6 - C7 - C31 = -4.2(14)
C11 - N3 - C8 - C7 = -176.8(8)
Zn1 - N3 - C8 - C7 = 1.4(12)
C11 - N3 - C8 - C9 = 0.7(9)
Zn1 - N3 - C8 - C9 = 178.9(6)
C6 - C7 - C8 - N3 = -4.8(15)
C31 - C7 - C8 - N3 = 177.8(8)
C6 - C7 - C8 - C9 = 178.0(9)
C31 - C7 - C8 - C9 = 0.5(13)
N3 - C8 - C9 - C10 = 1.1(10)
C7 - C8 - C9 - C10 = 178.6(9)
C8 - C9 - C10 - C11 = -2.4(10)
C8 - N3 - C11 - C12 = 176.4(9)
Zn1 - N3 - C11 - C12 = -1.8(12)
C8 - N3 - C11 - C10 = -2.2(9)
Zn1 - N3 - C11 - C10 = 179.6(6)
C9 - C10 - C11 - N3 = 2.9(10)
C9 - C10 - C11 - C12 = -175.7(9)
N3 - C11 - C12 - C13 = 10.7(14)
C10 - C11 - C12 - C13 = -170.9(9)
N3 - C11 - C12 - C41 = -169.7(7)
C10 - C11 - C12 - C41 = 8.7(13)
C11 - C12 - C13 - N4 = 3.9(14)
C41 - C12 - C13 - N4 = -175.7(7)
C11 - C12 - C13 - C14 = 175.6(9)
C41 - C12 - C13 - C14 = -4.0(14)
C16 - N4 - C13 - C12 = 173.0(8)
Zn1 - N4 - C13 - C12 = -25.4(12)
C16 - N4 - C13 - C14 = 0.0(9)
Zn1 - N4 - C13 - C14 = 161.7(6)
C12 - C13 - C14 - C15 = -171.1(9)
N4 - C13 - C14 - C15 = 1.7(11)
C13 - C14 - C15 - C16 = -2.7(11)
C13 - N4 - C16 - C17 = -178.5(8)
Zn1 - N4 - C16 - C17 = 20.2(12)
C13 - N4 - C16 - C15 = -1.7(9)
Zn1 - N4 - C16 - C15 = -162.9(6)
C14 - C15 - C16 - N4 = 2.8(10)
C14 - C15 - C16 - C17 = 179.6(9)
N4 - C16 - C17 - C18 = -5.5(14)
C15 - C16 - C17 - C18 = 178.1(9)

N4 - C16 - C17 - C51 = 172.5(8)
C15 - C16 - C17 - C51 = -3.9(13)
C1 - N1 - C18 - C17 = -173.7(9)
Zn1 - N1 - C18 - C17 = 3.9(13)
C1 - N1 - C18 - C19 = 2.0(9)
Zn1 - N1 - C18 - C19 = 179.5(5)
C16 - C17 - C18 - N1 = -7.4(15)
C51 - C17 - C18 - N1 = 174.7(8)
C16 - C17 - C18 - C19 = 177.7(9)
C51 - C17 - C18 - C19 = -0.2(14)
N1 - C18 - C19 - C20 = -3.6(10)
C17 - C18 - C19 - C20 = 172.1(9)
C18 - C19 - C20 - C1 = 3.6(10)
N1 - C1 - C20 - C19 = -2.5(10)
C2 - C1 - C20 - C19 = -178.6(9)
C1 - C2 - C21 - C22 = 66.1(13)
C3 - C2 - C21 - C22 = -116.3(11)
C1 - C2 - C21 - C26 = -113.8(10)
C3 - C2 - C21 - C26 = 63.7(12)
C26 - C21 - C22 - C23 = -2(2)
C2 - C21 - C22 - C23 = 177.6(12)
C21 - C22 - C23 - C24 = 4(2)
C22 - C23 - C24 - C25 = -4(2)
C23 - C24 - C25 - C26 = 1.3(19)
C24 - C25 - C26 - C21 = 0.6(15)
C22 - C21 - C26 - C25 = 0.0(15)
C2 - C21 - C26 - C25 = 180.0(8)
C6 - C7 - C31 - C32 = -103.1(11)
C8 - C7 - C31 - C32 = 74.5(12)
C6 - C7 - C31 - C36 = 74.6(13)
C8 - C7 - C31 - C36 = -107.7(11)
C36 - C31 - C32 - C33 = 0.0
C7 - C31 - C32 - C33 = 177.7(15)
C31 - C32 - C33 - C34 = 0.0
C32 - C33 - C34 - C35 = 0.0
C33 - C34 - C35 - C36 = 0.0
C34 - C35 - C36 - C31 = 0.0
C32 - C31 - C36 - C35 = 0.0
C7 - C31 - C36 - C35 = -177.8(15)
C13 - C12 - C41 - C42 = -121.2(9)
C11 - C12 - C41 - C42 = 59.2(11)
C13 - C12 - C41 - C46 = 58.6(11)
C11 - C12 - C41 - C46 = -121.0(9)
C46 - C41 - C42 - C43 = 0.3(11)

C12 - C41 - C42 - C43 = -179.8(7)
 C41 - C42 - C43 - C44 = -0.5(13)
 C42 - C43 - C44 - C45 = 0.7(14)
 C43 - C44 - C45 - C46 = -0.9(14)
 C44 - C45 - C46 - C41 = 0.7(13)
 C42 - C41 - C46 - C45 = -0.5(11)
 C12 - C41 - C46 - C45 = 179.7(7)
 C18 - C17 - C51 - C52 = 108.2(9)
 C16 - C17 - C51 - C52 = -69.9(11)
 C18 - C17 - C51 - C56 = -76.8(12)
 C16 - C17 - C51 - C56 = 105.1(10)
 C56 - C51 - C52 - C53 = 2.7(15)
 C17 - C51 - C52 - C53 = 177.7(9)
 C51 - C52 - C53 - C54 = -0.4(18)
 C52 - C53 - C54 - C55 = -2(2)
 C53 - C54 - C55 - C56 = 2(3)
 C54 - C55 - C56 - C57 = -165.2(16)
 C54 - C55 - C56 - C51 = 0(2)
 C52 - C51 - C56 - C57 = 162.0(13)
 C17 - C51 - C56 - C57 = -12.9(18)
 C52 - C51 - C56 - C55 = -2.7(17)
 C17 - C51 - C56 - C55 = -177.6(11)
 C55 - C56 - C57 - N58 = 20(2)
 C51 - C56 - C57 - N58 = -144.3(14)
 C55 - C56 - C57 - C61 = -144.2(15)
 C51 - C56 - C57 - C61 = 51(2)
 C56 - C57 - N58 - N59 = -171.5(15)
 C61 - C57 - N58 - N59 = -3.9(19)
 C57 - N58 - N59 - N60 = 3(2)
 N58 - N59 - N60 - C62 = 172.6(19)
 N58 - N59 - N60 - C61 = 0(2)
 C56 - C57 - C61 - N60 = 170.8(14)
 N58 - C57 - C61 - N60 = 4.0(19)
 C62 - N60 - C61 - C57 = -174(2)
 N59 - N60 - C61 - C57 = -2.2(18)
 C61 - N60 - C62 - C67 = -1(3)
 N59 - N60 - C62 - C67 = -171.7(17)
 C61 - N60 - C62 - N63 = -175.9(17)
 N59 - N60 - C62 - N63 = 14(3)
 N60 - C62 - N63 - C64 = -176.5(14)
 C67 - C62 - N63 - C64 = 10(2)
 C62 - N63 - C64 - C65 = -13(2)
 N63 - C64 - C65 - C66 = 20(3)
 C64 - C65 - C66 - C67 = -16(3)

$$N60 - C62 - C67 - C66 = 176.6(17)$$

$$N63 - C62 - C67 - C66 = -10(3)$$

$$C65 - C66 - C67 - C62 = 10(2)$$

$$C76 - N71 - C72 - C73 = 2.8(16)$$

$$Zn1 - N71 - C72 - C73 = -177.2(8)$$

$$N71 - C72 - C73 - C74 = -4.3(16)$$

$$C72 - C73 - C74 - C75 = 4.4(17)$$

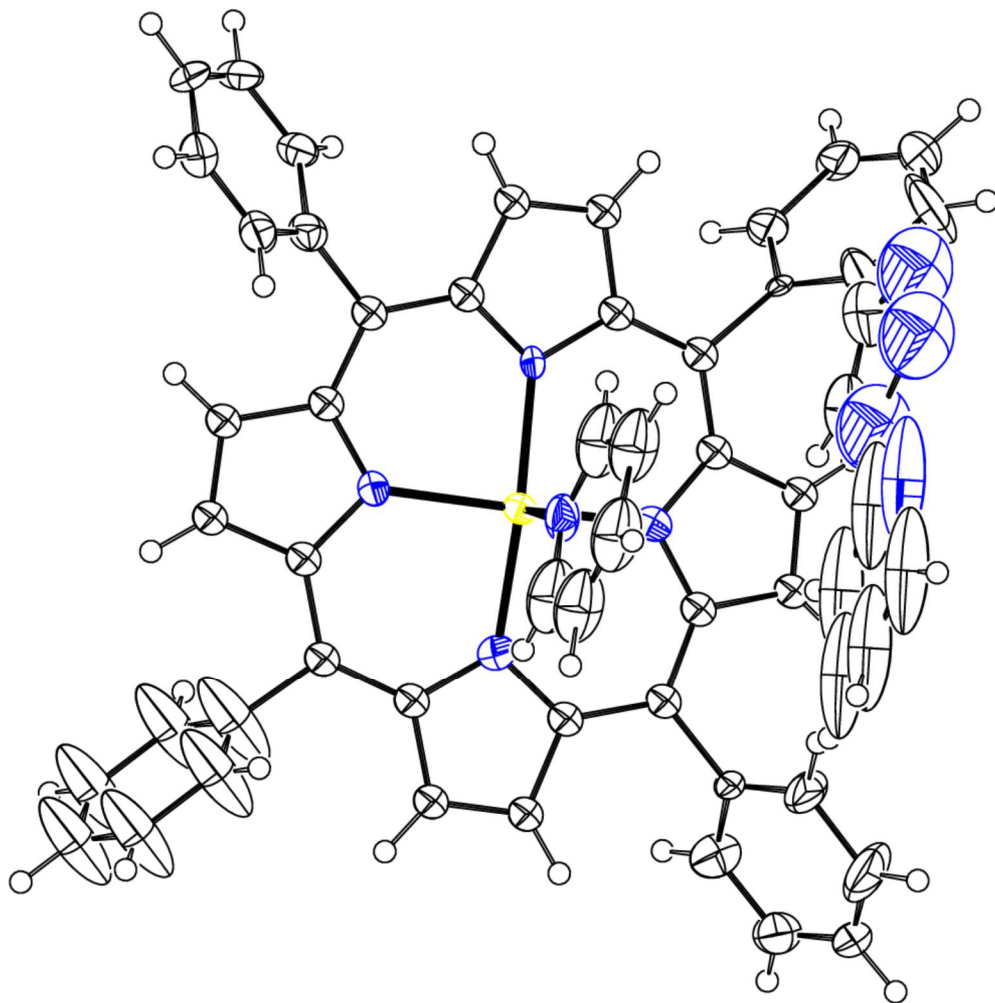
$$C73 - C74 - C75 - C76 = -3.0(19)$$

$$C72 - N71 - C76 - C75 = -1.3(17)$$

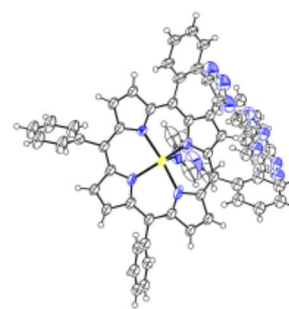
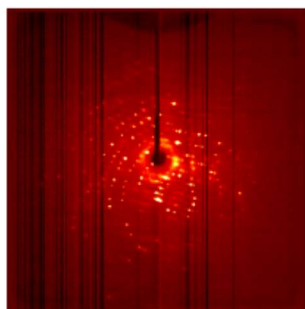
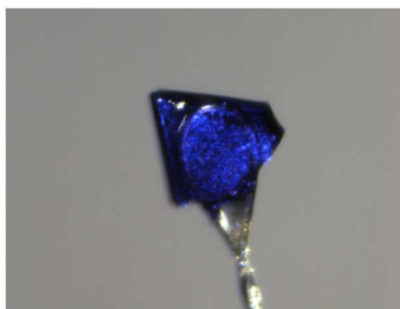
$$Zn1 - N71 - C76 - C75 = 178.8(9)$$

$$C74 - C75 - C76 - N71 = 1.4(19)$$

8.8. Structure visualization.



9. X-ray crystallographic data of [L·N-methylimidazole] CCDC-2061922.



($C_{55}H_{38}N_{10}Zn$); $M = 904.32$. A suitable crystal for X-ray diffraction single crystal experiment (violet prism, dimensions = 0.460 x 0.370 x 0.120 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector,^[*] using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator) at $T = 150(2) \text{ K}$. Crystal structure has been described in monoclinic symmetry and $P 2_1/c$ (I.T.#14) centric space group. Cell parameters have been founded as follows: $a = 14.3923(11)$, $b = 25.385(2)$, $c = 14.3762(13) \text{ \AA}$, $\beta = 107.782(3)^\circ$, $V = 5001.3(7) \text{ \AA}^3$. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.201 g.cm^{-3} and 0.537 mm^{-1} respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,^[17] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program).^[18] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,^[19] implemented as the *SQUEEZE* option in *PLATON*.^[20] A new data set, free of solvent contribution, was then used in the final refinement. All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 9953 unique intensities and 287 parameters converged at $\omega R(F^2) = 0.3296$ ($R_F = 0.1606$) for 7653 observed reflections with ($I > 2\sigma$). Due to the relatively poor quality of the crystal and its scattering power suggesting the presence of disorder in the crystallized compound, long exposition time was used for the measurement of the diffraction intensities. Despite these facts, the structural resolution evidenced unambiguously that the crystal crystallizes with one *N*-methylimidazole molecule coordinated to the Zn atom in the same face as the triazolopyridine fragment. The alert level B in the checkcif is due to the disordered triazolopyridine fragment and the poor quality of the sample.

[*] Thanks to FEDER funds.

9.1. Data data collection strategy details.

Software: BIS V6.2.1/2016-03-01
Number of scans: 2
Total number of frames [*]: 446
Total length of scans [*]: 223.00 (deg.)
Rotation speed [*]: 80.00 sec./deg.
Total exposition time [*]: 4 h 57.3 min.

[*] fast scan not included

Measurement mode: shutterless mode

Scan	Time(s)	Width	DX (mm)	Frames	Theta	Omega	Phi	Chi	T(K)
1 Phi	40.0	0.50	34.0	446	0.27	270.94	256.51	23.00	150.02
2 Fast	8.0	1.00	34.0	180	0.00	360.00	0.00	54.74	150.00

9.2. Structural data.

... Crystal data ...

Empirical formula	C ₅₅ H ₃₈ N ₁₀ Zn
Formula weight	904.32 g/mol
Temperature	150(2) K
Radiation type	Mo-K α
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ /c
Unit cell dimensions	a = 14.3923(11) Å b = 25.385(2) Å c = 14.3762(13) Å β = 107.782(3) °
Volume	5001.3(7) Å ³
Z, Calculated density	4, 1.201 g.cm ⁻³
Absorption coefficient	0.537 mm ⁻¹
F(000)	1872
Crystal size	0.460 x 0.370 x 0.120 mm
Crystal color	violet
Crystal description	prism

... Data collection ...

Diffractometer	D8 Venture diffractometer
θ range for data collection	2.829 to 26.370 °
$(\sin \theta / \lambda)_{\max}$ (Å ⁻¹)	0.625
h_{\min}, h_{\max}	-17, 17
k_{\min}, k_{\max}	-31, 31
l_{\min}, l_{\max}	-17, 17
Reflections collected / unique	34089 / 9953 [R(int) = 0.0616]
Reflections [$I > 2\sigma$]	7653
Completeness to θ_{\max}	0.975
Absorption correction type	multi-scan
Max. and min. transmission	0.938 , 0.669

... Refinement ...

Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	9953 / 0 / 287
Goodness-of-fit	1.056
Final R indices [$I > 2\sigma$]	$R_1 = 0.1606$, $\omega R_2 = 0.3296$
R indices (all data)	$R_1 = 0.1881$, $\omega R_2 = 0.3452$
$\Delta\rho_{\max}, \Delta\rho_{\min}$	0.960, -1.038 e.Å ⁻³

9.3. Fractional atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (\AA^2).

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	occ.	$U(\text{eq})$	adp
Zn1	0.37101(7)	0.65660(4)	0.49912(7)	1	0.0403(3)	Uani
N1	0.4247(5)	0.6704(3)	0.6481(5)	1	0.0374(16)	Uani
N2	0.5080(5)	0.6751(3)	0.4871(5)	1	0.0408(17)	Uani
N3	0.3150(5)	0.6677(3)	0.3483(6)	1	0.052(2)	Uani
N4	0.2322(5)	0.6700(3)	0.5095(5)	1	0.0403(16)	Uani
C1	0.5218(6)	0.6758(4)	0.7013(6)	1	0.0465(5)	Uani
C2	0.5992(6)	0.6828(4)	0.6633(6)	1	0.0465(5)	Uani
C3	0.5902(6)	0.6837(4)	0.5622(6)	1	0.0465(5)	Uani
C4	0.6698(6)	0.6931(4)	0.5219(6)	1	0.0465(5)	Uani
H4	0.735273	0.701392	0.558109	1	0.056	Uiso
C5	0.6348(6)	0.6881(4)	0.4251(6)	1	0.0465(5)	Uani
H5	0.670325	0.692011	0.379632	1	0.056	Uiso
C6	0.5327(6)	0.6757(4)	0.4027(6)	1	0.0465(5)	Uani
C7	0.4686(6)	0.6675(4)	0.3070(6)	1	0.0465(5)	Uani
C8	0.3670(6)	0.6632(4)	0.2846(6)	1	0.0465(5)	Uani
C9	0.3004(6)	0.6555(4)	0.1877(6)	1	0.0465(5)	Uani
H9	0.317860	0.650274	0.129729	1	0.056	Uiso
C10	0.2109(6)	0.6569(4)	0.1940(6)	1	0.0465(5)	Uani
H10	0.152414	0.653462	0.141211	1	0.056	Uiso
C11	0.2177(6)	0.6648(4)	0.2970(6)	1	0.0465(5)	Uani
C12	0.1412(6)	0.6692(4)	0.3348(6)	1	0.0465(5)	Uani
C13	0.1457(6)	0.6742(4)	0.4337(6)	1	0.0465(5)	Uani
C14	0.0665(6)	0.6792(4)	0.4716(6)	1	0.0465(5)	Uani
H14	-0.000119	0.683065	0.434501	1	0.056	Uiso
C15	0.1020(6)	0.6774(4)	0.5695(6)	1	0.0465(5)	Uani
H15	0.065692	0.679358	0.614570	1	0.056	Uiso
C16	0.2062(6)	0.6719(4)	0.5923(6)	1	0.0465(5)	Uani
C17	0.2709(6)	0.6654(4)	0.6885(6)	1	0.0465(5)	Uani
C18	0.3732(6)	0.6663(4)	0.7113(6)	1	0.0465(5)	Uani
C19	0.4396(6)	0.6673(4)	0.8109(6)	1	0.0465(5)	Uani
H19	0.422278	0.663453	0.869225	1	0.056	Uiso
C20	0.5300(6)	0.6746(4)	0.8043(6)	1	0.0465(5)	Uani
H20	0.588318	0.678333	0.857290	1	0.056	Uiso
C21	0.6989(4)	0.6918(3)	0.7379(5)	1	0.049(2)	Uani
C22	0.7514(5)	0.6504(2)	0.7925(5)	1	0.0791(17)	Uani
H22	0.723226	0.616236	0.787187	1	0.095	Uiso
C23	0.8451(5)	0.6589(3)	0.8550(6)	1	0.0791(17)	Uani
H23	0.880995	0.630552	0.892295	1	0.095	Uiso

C24	0.8864(4)	0.7088(3)	0.8628(5)	1	0.0791(17)	Uani
H24	0.950408	0.714648	0.905449	1	0.095	Uiso
C25	0.8339(5)	0.7503(2)	0.8082(6)	1	0.0791(17)	Uani
H25	0.862052	0.784429	0.813496	1	0.095	Uiso
C26	0.7402(5)	0.7418(2)	0.7457(5)	1	0.0791(17)	Uani
H26	0.704283	0.770114	0.708387	1	0.095	Uiso
C31	0.5133(5)	0.6620(3)	0.2257(4)	1	0.0615(12)	Uani
C32	0.5798(5)	0.6217(3)	0.2298(4)	1	0.0615(12)	Uani
H32	0.597675	0.598558	0.284264	1	0.074	Uiso
C33	0.6201(4)	0.6153(2)	0.1541(5)	1	0.0615(12)	Uani
H33	0.665586	0.587755	0.156910	1	0.074	Uiso
C34	0.5940(5)	0.6492(3)	0.0744(4)	1	0.0615(12)	Uani
H34	0.621541	0.644804	0.022683	1	0.074	Uiso
C35	0.5275(5)	0.6895(3)	0.0703(4)	1	0.0615(12)	Uani
H35	0.509585	0.712657	0.015809	1	0.074	Uiso
C36	0.4871(4)	0.6959(3)	0.1460(5)	1	0.0615(12)	Uani
H36	0.441673	0.723461	0.143162	1	0.074	Uiso
C41A	0.0406(4)	0.6694(4)	0.2619(5)	0.628(7)	0.0780(15)	Uani
C42A	0.0154(5)	0.7117(3)	0.1979(5)	0.628(7)	0.0780(15)	Uani
H42A	0.059093	0.740490	0.204181	0.628(7)	0.094	Uiso
C43A	-0.0738(5)	0.7120(3)	0.1246(5)	0.628(7)	0.0780(15)	Uani
H43A	-0.091070	0.740985	0.080804	0.628(7)	0.094	Uiso
C44A	-0.1378(4)	0.6699(3)	0.1153(5)	0.628(7)	0.0780(15)	Uani
H44A	-0.198806	0.670151	0.065236	0.628(7)	0.094	Uiso
C45A	-0.1126(5)	0.6276(3)	0.1794(5)	0.628(7)	0.0780(15)	Uani
H45A	-0.156378	0.598821	0.173044	0.628(7)	0.094	Uiso
C46A	-0.0234(5)	0.6273(3)	0.2527(5)	0.628(7)	0.0780(15)	Uani
H46A	-0.006215	0.598324	0.296422	0.628(7)	0.094	Uiso
C51A	0.2267(6)	0.6570(4)	0.7702(5)	0.628(7)	0.0364(18)	Uani
C52A	0.2346(8)	0.6962(5)	0.8419(7)	0.628(7)	0.0620(12)	Uani
H52A	0.268543	0.728065	0.839618	0.628(7)	0.074	Uiso
C53A	0.1928(8)	0.6880(5)	0.9154(7)	0.628(7)	0.0620(12)	Uani
H53A	0.197929	0.714622	0.963177	0.628(7)	0.074	Uiso
C54A	0.1449(8)	0.6429(5)	0.9205(7)	0.628(7)	0.0620(12)	Uani
H54A	0.115586	0.638722	0.970997	0.628(7)	0.074	Uiso
C55A	0.1374(8)	0.6020(5)	0.8527(7)	0.628(7)	0.0620(12)	Uani
H55A	0.106350	0.569643	0.858288	0.628(7)	0.074	Uiso
C56A	0.1778(8)	0.6109(5)	0.7759(7)	0.628(7)	0.0620(12)	Uani
C57A	0.1812(13)	0.5591(8)	0.7193(11)	0.314(3)	0.0620(12)	Uani
C58A	0.1549(13)	0.5533(8)	0.6199(12)	0.314(3)	0.0620(12)	Uani
H58A	0.137768	0.581184	0.573740	0.314(3)	0.074	Uiso
N59A	0.1571(14)	0.5011(6)	0.5974(15)	0.314(3)	0.076(3)	Uani
N60A	0.1855(13)	0.4731(6)	0.6893(13)	0.314(3)	0.076(3)	Uani
N61A	0.2001(12)	0.5093(6)	0.7566(13)	0.314(3)	0.076(3)	Uani

C62A	0.134(3)	0.4743(13)	0.527(2)	0.314(3)	0.067(4)	Uani
C63A	0.098(3)	0.4997(9)	0.437(3)	0.314(3)	0.067(4)	Uani
H63A	0.093035	0.537033	0.434868	0.314(3)	0.080	Uiso
C64A	0.071(2)	0.4706(11)	0.351(2)	0.314(3)	0.067(4)	Uani
H64A	0.046242	0.487971	0.290182	0.314(3)	0.080	Uiso
C65A	0.0787(18)	0.4160(10)	0.3549(15)	0.314(3)	0.067(4)	Uani
H65A	0.059702	0.396083	0.296113	0.314(3)	0.080	Uiso
C66A	0.1145(19)	0.3906(9)	0.4443(18)	0.314(3)	0.067(4)	Uani
H66A	0.119954	0.353256	0.446730	0.314(3)	0.080	Uiso
N67A	0.142(2)	0.4197(13)	0.5303(15)	0.314(3)	0.067(4)	Uani
C57B	0.1812(13)	0.5591(8)	0.7193(11)	0.314(3)	0.0620(12)	Uani
C58B	0.1549(13)	0.5533(8)	0.6199(12)	0.314(3)	0.0620(12)	Uani
H58B	0.137768	0.581184	0.573740	0.314(3)	0.074	Uiso
N59B	0.1571(14)	0.5011(6)	0.5974(15)	0.314(3)	0.076(3)	Uani
N60B	0.1855(13)	0.4731(6)	0.6893(13)	0.314(3)	0.076(3)	Uani
N61B	0.2001(12)	0.5093(6)	0.7566(13)	0.314(3)	0.076(3)	Uani
C62B	0.132(2)	0.4720(12)	0.5098(19)	0.314(3)	0.067(4)	Uani
C63B	0.106(2)	0.5068(9)	0.431(3)	0.314(3)	0.067(4)	Uani
H63B	0.101757	0.543454	0.442518	0.314(3)	0.080	Uiso
C64B	0.086(2)	0.4879(9)	0.337(2)	0.314(3)	0.067(4)	Uani
H64B	0.068794	0.511598	0.282967	0.314(3)	0.080	Uiso
C65B	0.0927(16)	0.4342(10)	0.3203(16)	0.314(3)	0.067(4)	Uani
H65B	0.079351	0.421252	0.255489	0.314(3)	0.080	Uiso
C66B	0.1186(17)	0.3994(9)	0.3987(17)	0.314(3)	0.067(4)	Uani
H66B	0.122871	0.362761	0.387561	0.314(3)	0.080	Uiso
N67B	0.1382(19)	0.4184(11)	0.4935(16)	0.314(3)	0.067(4)	Uani
C41B	0.0406(4)	0.6694(4)	0.2619(5)	0.372(7)	0.0780(15)	Uani
C42B	0.0154(5)	0.7117(3)	0.1979(5)	0.372(7)	0.0780(15)	Uani
H42B	0.059093	0.740490	0.204181	0.372(7)	0.094	Uiso
C43B	-0.0738(5)	0.7120(3)	0.1246(5)	0.372(7)	0.0780(15)	Uani
H43B	-0.091070	0.740985	0.080804	0.372(7)	0.094	Uiso
C44B	-0.1378(4)	0.6699(3)	0.1153(5)	0.372(7)	0.0780(15)	Uani
H44B	-0.198806	0.670151	0.065236	0.372(7)	0.094	Uiso
C45B	-0.1126(5)	0.6276(3)	0.1794(5)	0.372(7)	0.0780(15)	Uani
H45B	-0.156378	0.598821	0.173044	0.372(7)	0.094	Uiso
C46B	-0.0234(5)	0.6273(3)	0.2527(5)	0.372(7)	0.0780(15)	Uani
C51B	0.2267(6)	0.6570(4)	0.7702(5)	0.372(7)	0.0364(18)	Uani
C52B	0.2346(8)	0.6962(5)	0.8419(7)	0.372(7)	0.0620(12)	Uani
H52B	0.268543	0.728065	0.839618	0.372(7)	0.074	Uiso
C53B	0.1928(8)	0.6880(5)	0.9154(7)	0.372(7)	0.0620(12)	Uani
H53B	0.197929	0.714622	0.963177	0.372(7)	0.074	Uiso
C54B	0.1449(8)	0.6429(5)	0.9205(7)	0.372(7)	0.0620(12)	Uani
H54B	0.115586	0.638722	0.970997	0.372(7)	0.074	Uiso
C55B	0.1374(8)	0.6020(5)	0.8527(7)	0.372(7)	0.0620(12)	Uani

H55B	0.106350	0.569643	0.858288	0.372(7)	0.074	Uiso
C56B	0.1778(8)	0.6109(5)	0.7759(7)	0.372(7)	0.0620(12)	Uani
H56B	0.171214	0.584647	0.727216	0.372(7)	0.074	Uiso
C81	0.006(2)	0.5769(15)	0.286(2)	0.372(7)	0.0780(15)	Uani
N82	-0.0398(18)	0.5362(13)	0.2288(18)	0.372(7)	0.0780(15)	Uani
N83	-0.0051(18)	0.4943(13)	0.2836(18)	0.372(7)	0.0780(15)	Uani
N84	0.0587(19)	0.5081(14)	0.374(2)	0.372(7)	0.0780(15)	Uani
C85	0.062(2)	0.5657(16)	0.368(2)	0.372(7)	0.0780(15)	Uani
H85	0.099538	0.589346	0.416400	0.372(7)	0.094	Uiso
C86	0.097(3)	0.4789(18)	0.450(2)	0.372(7)	0.0780(15)	Uani
N87	0.0872(18)	0.4205(14)	0.4282(19)	0.372(7)	0.0780(15)	Uani
C88	0.138(2)	0.3873(18)	0.512(2)	0.372(7)	0.0780(15)	Uani
H88	0.145177	0.350446	0.504280	0.372(7)	0.094	Uiso
C89	0.175(2)	0.4102(16)	0.599(2)	0.372(7)	0.0780(15)	Uani
H89	0.198239	0.388997	0.655561	0.372(7)	0.094	Uiso
C90	0.180(2)	0.4693(19)	0.608(3)	0.372(7)	0.0780(15)	Uani
H90	0.209218	0.487104	0.667639	0.372(7)	0.094	Uiso
C91	0.139(3)	0.4940(19)	0.525(3)	0.372(7)	0.0780(15)	Uani
H91	0.145296	0.531218	0.529280	0.372(7)	0.094	Uiso
N71	0.3717(6)	0.5742(3)	0.4968(7)	1	0.056(2)	Uani
C72	0.4006(11)	0.5405(5)	0.5781(15)	1	0.104(3)	Uani
H72	0.421759	0.550967	0.644750	1	0.125	Uiso
C73	0.3927(11)	0.4906(6)	0.5443(15)	1	0.104(3)	Uani
H73	0.407072	0.459631	0.583100	1	0.125	Uiso
N74	0.3631(9)	0.4922(5)	0.4528(12)	1	0.104(3)	Uani
C75	0.3483(11)	0.5429(5)	0.4228(15)	1	0.104(3)	Uani
H75	0.324052	0.553864	0.356593	1	0.125	Uiso
C76	0.3466(11)	0.4470(5)	0.3858(14)	1	0.104(3)	Uani
H76A	0.323498	0.459607	0.318203	1	0.156	Uiso
H76B	0.407840	0.427616	0.396299	1	0.156	Uiso
H76C	0.297486	0.423670	0.398287	1	0.156	Uiso

9.4. Anisotropic displacement parameters (\AA^2).

The anisotropic displacement factor exponent takes the form: $-2\pi[h^2a^{*2}U_{11}+\dots +2hka^*b^*U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
Zn1	0.0331(5)	0.0483(6)	0.0330(5)	-0.0100(4)	0.0006(4)	-0.0041(4)
N1	0.035(4)	0.050(4)	0.025(3)	-0.011(3)	0.005(3)	-0.006(3)
N2	0.033(4)	0.048(4)	0.034(4)	-0.004(3)	-0.001(3)	-0.006(3)
N3	0.035(4)	0.066(5)	0.044(4)	-0.013(4)	-0.005(3)	-0.005(4)
N4	0.033(4)	0.049(4)	0.032(4)	-0.008(3)	0.000(3)	-0.001(3)
C1	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C2	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)

C3	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C4	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C5	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C6	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C7	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C8	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C9	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C10	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C11	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C12	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C13	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C14	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C15	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C16	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C17	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C18	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C19	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C20	0.0356(10)	0.0658(13)	0.0326(10)	-0.0122(9)	0.0022(8)	-0.0040(9)
C21	0.035(5)	0.075(7)	0.035(5)	0.001(4)	0.009(4)	-0.002(4)
C22	0.057(3)	0.086(4)	0.070(3)	-0.003(3)	-0.016(3)	-0.002(3)
C23	0.057(3)	0.086(4)	0.070(3)	-0.003(3)	-0.016(3)	-0.002(3)
C24	0.057(3)	0.086(4)	0.070(3)	-0.003(3)	-0.016(3)	-0.002(3)
C25	0.057(3)	0.086(4)	0.070(3)	-0.003(3)	-0.016(3)	-0.002(3)
C26	0.057(3)	0.086(4)	0.070(3)	-0.003(3)	-0.016(3)	-0.002(3)
C31	0.047(2)	0.088(3)	0.048(2)	-0.014(2)	0.012(2)	-0.016(2)
C32	0.047(2)	0.088(3)	0.048(2)	-0.014(2)	0.012(2)	-0.016(2)
C33	0.047(2)	0.088(3)	0.048(2)	-0.014(2)	0.012(2)	-0.016(2)
C34	0.047(2)	0.088(3)	0.048(2)	-0.014(2)	0.012(2)	-0.016(2)
C35	0.047(2)	0.088(3)	0.048(2)	-0.014(2)	0.012(2)	-0.016(2)
C36	0.047(2)	0.088(3)	0.048(2)	-0.014(2)	0.012(2)	-0.016(2)
C41A	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C42A	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C43A	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C44A	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C45A	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C46A	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C51A	0.033(4)	0.057(5)	0.017(3)	-0.006(3)	0.005(3)	-0.001(4)
C52A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C53A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C54A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C55A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C56A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C57A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C58A	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)

N59A	0.084(7)	0.052(5)	0.090(8)	0.011(5)	0.024(6)	-0.005(5)
N60A	0.084(7)	0.052(5)	0.090(8)	0.011(5)	0.024(6)	-0.005(5)
N61A	0.084(7)	0.052(5)	0.090(8)	0.011(5)	0.024(6)	-0.005(5)
C62A	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C63A	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C64A	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C65A	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C66A	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
N67A	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C57B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C58B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
N59B	0.084(7)	0.052(5)	0.090(8)	0.011(5)	0.024(6)	-0.005(5)
N60B	0.084(7)	0.052(5)	0.090(8)	0.011(5)	0.024(6)	-0.005(5)
N61B	0.084(7)	0.052(5)	0.090(8)	0.011(5)	0.024(6)	-0.005(5)
C62B	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C63B	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C64B	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C65B	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C66B	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
N67B	0.051(5)	0.088(7)	0.068(9)	-0.038(7)	0.027(6)	-0.010(5)
C41B	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C42B	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C43B	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C44B	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C45B	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C46B	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C51B	0.033(4)	0.057(5)	0.017(3)	-0.006(3)	0.005(3)	-0.001(4)
C52B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C53B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C54B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C55B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C56B	0.062(3)	0.089(3)	0.035(2)	-0.015(2)	0.015(2)	0.001(2)
C81	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
N82	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
N83	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
N84	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C85	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C86	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
N87	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C88	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C89	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C90	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
C91	0.048(2)	0.130(4)	0.048(2)	0.005(2)	0.0028(19)	-0.017(2)
N71	0.034(4)	0.054(5)	0.080(6)	-0.013(5)	0.020(4)	-0.004(4)

C72	0.084(4)	0.057(3)	0.187(8)	-0.020(5)	0.067(5)	-0.005(3)
C73	0.084(4)	0.057(3)	0.187(8)	-0.020(5)	0.067(5)	-0.005(3)
N74	0.084(4)	0.057(3)	0.187(8)	-0.020(5)	0.067(5)	-0.005(3)
C75	0.084(4)	0.057(3)	0.187(8)	-0.020(5)	0.067(5)	-0.005(3)
C76	0.084(4)	0.057(3)	0.187(8)	-0.020(5)	0.067(5)	-0.005(3)

9.5. Bond length [Å].

Zn1 - N1 = 2.073(6)
 Zn1 - N4 = 2.077(7)
 Zn1 - N2 = 2.084(7)
 Zn1 - N3 = 2.089(8)
 Zn1 - N71 = 2.093(8)
 N1 - C18 = 1.341(11)
 N1 - C1 = 1.380(10)
 N2 - C3 = 1.354(10)
 N2 - C6 = 1.366(11)
 N3 - C8 = 1.354(12)
 N3 - C11 = 1.370(11)
 N4 - C16 = 1.352(11)
 N4 - C13 = 1.387(10)
 C1 - C2 = 1.393(13)
 C1 - C20 = 1.449(12)
 C2 - C3 = 1.420(12)
 C2 - C21 = 1.525(9)
 C3 - C4 = 1.453(13)
 C4 - C5 = 1.334(12)
 C4 - H4 = 0.9500
 C5 - C6 = 1.439(12)
 C5 - H5 = 0.9500
 C6 - C7 = 1.419(11)
 C7 - C8 = 1.401(12)
 C7 - C31 = 1.503(10)
 C8 - C9 = 1.443(11)
 C9 - C10 = 1.319(12)
 C9 - H9 = 0.9500
 C10 - C11 = 1.468(12)
 C10 - H10 = 0.9500
 C11 - C12 = 1.373(13)
 C12 - C13 = 1.409(12)
 C12 - C41A = 1.507(9)
 C12 - C41B = 1.507(9)
 C13 - C14 = 1.411(13)
 C14 - C15 = 1.342(12)
 C14 - H14 = 0.9500

C15 - C16 = 1.441(12)
C15 - H15 = 0.9500
C16 - C17 = 1.422(12)
C17 - C18 = 1.408(12)
C17 - C51B = 1.511(12)
C17 - C51A = 1.511(12)
C18 - C19 = 1.458(11)
C19 - C20 = 1.347(12)
C19 - H19 = 0.9500
C20 - H20 = 0.9500
C21 - C22 = 1.3900
C21 - C26 = 1.3900
C22 - C23 = 1.3900
C22 - H22 = 0.9500
C23 - C24 = 1.3900
C23 - H23 = 0.9500
C24 - C25 = 1.3900
C24 - H24 = 0.9500
C25 - C26 = 1.3900
C25 - H25 = 0.9500
C26 - H26 = 0.9500
C31 - C32 = 1.3900
C31 - C36 = 1.3900
C32 - C33 = 1.3900
C32 - H32 = 0.9500
C33 - C34 = 1.3900
C33 - H33 = 0.9500
C34 - C35 = 1.3900
C34 - H34 = 0.9500
C35 - C36 = 1.3900
C35 - H35 = 0.9500
C36 - H36 = 0.9500
C41A - C42A = 1.3900
C41A - C46A = 1.3900
C42A - C43A = 1.3900
C42A - H42A = 0.9500
C43A - C44A = 1.3900
C43A - H43A = 0.9500
C44A - C45A = 1.3900
C44A - H44A = 0.9500
C45A - C46A = 1.3900
C45A - H45A = 0.9500
C46A - H46A = 0.9500
C51A - C56A = 1.381(14)

C51A - C52A = 1.412(13)
C52A - C53A = 1.382(14)
C52A - H52A = 0.9500
C53A - C54A = 1.351(16)
C53A - H53A = 0.9500
C54A - C55A = 1.405(14)
C54A - H54A = 0.9500
C55A - C56A = 1.416(14)
C55A - H55A = 0.9500
C56A - C57A = 1.56(2)
C57A - N61A = 1.37(2)
C57A - C58A = 1.37(2)
C58A - N59A = 1.37(2)
C58A - H58A = 0.9500
N59A - C62A = 1.18(3)
N59A - N60A = 1.44(2)
N60A - N61A = 1.30(2)
C62A - C63A = 1.3900
C62A - N67A = 1.3900
C63A - C64A = 1.3900
C63A - H63A = 0.9500
C64A - C65A = 1.3900
C64A - H64A = 0.9500
C65A - C66A = 1.3900
C65A - H65A = 0.9500
C66A - N67A = 1.3900
C66A - H66A = 0.9500
C57B - N61B = 1.37(2)
C57B - C58B = 1.37(2)
C58B - N59B = 1.37(2)
C58B - H58B = 0.9500
N59B - C62B = 1.41(3)
N59B - N60B = 1.44(2)
N60B - N61B = 1.30(2)
C62B - C63B = 1.3900
C62B - N67B = 1.3900
C63B - C64B = 1.3900
C63B - H63B = 0.9500
C64B - C65B = 1.3900
C64B - H64B = 0.9500
C65B - C66B = 1.3900
C65B - H65B = 0.9500
C66B - N67B = 1.3900
C66B - H66B = 0.9500

C41B - C42B = 1.3900
C41B - C46B = 1.3900
C42B - C43B = 1.3900
C42B - H42B = 0.9500
C43B - C44B = 1.3900
C43B - H43B = 0.9500
C44B - C45B = 1.3900
C44B - H44B = 0.9500
C45B - C46B = 1.3900
C45B - H45B = 0.9500
C46B - C81 = 1.39(4)
C51B - C56B = 1.381(14)
C51B - C52B = 1.412(13)
C52B - C53B = 1.382(14)
C52B - H52B = 0.9500
C53B - C54B = 1.351(16)
C53B - H53B = 0.9500
C54B - C55B = 1.405(14)
C54B - H54B = 0.9500
C55B - C56B = 1.416(14)
C55B - H55B = 0.9500
C56B - H56B = 0.9500
C81 - C85 = 1.24(4)
C81 - N82 = 1.36(4)
N82 - N83 = 1.33(4)
N83 - N84 = 1.39(3)
N84 - C86 = 1.29(4)
N84 - C85 = 1.47(5)
C85 - H85 = 0.9500
C86 - C91 = 1.13(5)
C86 - N87 = 1.51(5)
N87 - C88 = 1.47(4)
C88 - C89 = 1.33(5)
C88 - H88 = 0.9500
C89 - C90 = 1.51(5)
C89 - H89 = 0.9500
C90 - C91 = 1.31(5)
C90 - H90 = 0.9500
C91 - H91 = 0.9500
N71 - C75 = 1.286(18)
N71 - C72 = 1.405(19)
C72 - C73 = 1.349(18)
C72 - H72 = 0.9500
C73 - N74 = 1.25(2)

C73 - H73 = 0.9500
N74 - C75 = 1.354(18)
N74 - C76 = 1.469(18)
C75 - H75 = 0.9500
C76 - H76A = 0.9800
C76 - H76B = 0.9800
C76 - H76C = 0.9800

9.6. Angles [°].

N1 - Zn1 - N4 = 87.8(3)
N1 - Zn1 - N2 = 89.1(3)
N4 - Zn1 - N2 = 157.5(3)
N1 - Zn1 - N3 = 162.5(3)
N4 - Zn1 - N3 = 88.7(3)
N2 - Zn1 - N3 = 87.7(3)
N1 - Zn1 - N71 = 100.6(3)
N4 - Zn1 - N71 = 100.0(3)
N2 - Zn1 - N71 = 102.4(3)
N3 - Zn1 - N71 = 96.9(4)
C18 - N1 - C1 = 107.9(7)
C18 - N1 - Zn1 = 125.3(5)
C1 - N1 - Zn1 = 125.8(6)
C3 - N2 - C6 = 107.7(7)
C3 - N2 - Zn1 = 126.1(6)
C6 - N2 - Zn1 = 125.9(5)
C8 - N3 - C11 = 108.5(7)
C8 - N3 - Zn1 = 125.0(6)
C11 - N3 - Zn1 = 124.0(7)
C16 - N4 - C13 = 105.4(7)
C16 - N4 - Zn1 = 126.9(6)
C13 - N4 - Zn1 = 127.5(6)
N1 - C1 - C2 = 126.2(8)
N1 - C1 - C20 = 108.5(8)
C2 - C1 - C20 = 125.3(8)
C1 - C2 - C3 = 124.8(8)
C1 - C2 - C21 = 115.9(7)
C3 - C2 - C21 = 119.3(8)
N2 - C3 - C2 = 126.6(9)
N2 - C3 - C4 = 108.3(8)
C2 - C3 - C4 = 125.1(8)
C5 - C4 - C3 = 107.9(8)
C5 - C4 - H4 = 126.1
C3 - C4 - H4 = 126.1
C4 - C5 - C6 = 106.8(8)

C4 - C5 - H5 = 126.6
C6 - C5 - H5 = 126.6
N2 - C6 - C7 = 126.3(8)
N2 - C6 - C5 = 109.2(7)
C7 - C6 - C5 = 124.5(9)
C8 - C7 - C6 = 123.9(8)
C8 - C7 - C31 = 118.6(7)
C6 - C7 - C31 = 117.5(8)
N3 - C8 - C7 = 126.3(8)
N3 - C8 - C9 = 108.8(8)
C7 - C8 - C9 = 124.8(8)
C10 - C9 - C8 = 107.7(8)
C10 - C9 - H9 = 126.1
C8 - C9 - H9 = 126.1
C9 - C10 - C11 = 107.9(8)
C9 - C10 - H10 = 126.0
C11 - C10 - H10 = 126.0
N3 - C11 - C12 = 126.4(8)
N3 - C11 - C10 = 107.0(8)
C12 - C11 - C10 = 126.6(8)
C11 - C12 - C13 = 127.7(8)
C11 - C12 - C41A = 116.2(8)
C13 - C12 - C41A = 116.0(8)
C11 - C12 - C41B = 116.2(8)
C13 - C12 - C41B = 116.0(8)
N4 - C13 - C12 = 122.7(8)
N4 - C13 - C14 = 109.9(8)
C12 - C13 - C14 = 127.3(8)
C15 - C14 - C13 = 108.0(8)
C15 - C14 - H14 = 126.0
C13 - C14 - H14 = 126.0
C14 - C15 - C16 = 106.1(8)
C14 - C15 - H15 = 126.9
C16 - C15 - H15 = 126.9
N4 - C16 - C17 = 125.3(8)
N4 - C16 - C15 = 110.6(7)
C17 - C16 - C15 = 124.0(8)
C18 - C17 - C16 = 123.5(9)
C18 - C17 - C51B = 118.7(7)
C16 - C17 - C51B = 117.8(8)
C18 - C17 - C51A = 118.7(7)
C16 - C17 - C51A = 117.8(8)
N1 - C18 - C17 = 126.8(8)
N1 - C18 - C19 = 109.4(7)

C17 - C18 - C19 = 123.6(8)
C20 - C19 - C18 = 106.9(8)
C20 - C19 - H19 = 126.5
C18 - C19 - H19 = 126.5
C19 - C20 - C1 = 107.2(8)
C19 - C20 - H20 = 126.4
C1 - C20 - H20 = 126.4
C22 - C21 - C26 = 120.0
C22 - C21 - C2 = 121.0(6)
C26 - C21 - C2 = 118.8(6)
C23 - C22 - C21 = 120.0
C23 - C22 - H22 = 120.0
C21 - C22 - H22 = 120.0
C22 - C23 - C24 = 120.0
C22 - C23 - H23 = 120.0
C24 - C23 - H23 = 120.0
C23 - C24 - C25 = 120.0
C23 - C24 - H24 = 120.0
C25 - C24 - H24 = 120.0
C26 - C25 - C24 = 120.0
C26 - C25 - H25 = 120.0
C24 - C25 - H25 = 120.0
C25 - C26 - C21 = 120.0
C25 - C26 - H26 = 120.0
C21 - C26 - H26 = 120.0
C32 - C31 - C36 = 120.0
C32 - C31 - C7 = 119.2(6)
C36 - C31 - C7 = 120.8(6)
C33 - C32 - C31 = 120.0
C33 - C32 - H32 = 120.0
C31 - C32 - H32 = 120.0
C34 - C33 - C32 = 120.0
C34 - C33 - H33 = 120.0
C32 - C33 - H33 = 120.0
C35 - C34 - C33 = 120.0
C35 - C34 - H34 = 120.0
C33 - C34 - H34 = 120.0
C36 - C35 - C34 = 120.0
C36 - C35 - H35 = 120.0
C34 - C35 - H35 = 120.0
C35 - C36 - C31 = 120.0
C35 - C36 - H36 = 120.0
C31 - C36 - H36 = 120.0
C42A - C41A - C46A = 120.0

C42A - C41A - C12 = 117.6(6)
C46A - C41A - C12 = 122.2(6)
C41A - C42A - C43A = 120.0
C41A - C42A - H42A = 120.0
C43A - C42A - H42A = 120.0
C44A - C43A - C42A = 120.0
C44A - C43A - H43A = 120.0
C42A - C43A - H43A = 120.0
C45A - C44A - C43A = 120.0
C45A - C44A - H44A = 120.0
C43A - C44A - H44A = 120.0
C44A - C45A - C46A = 120.0
C44A - C45A - H45A = 120.0
C46A - C45A - H45A = 120.0
C45A - C46A - C41A = 120.0
C45A - C46A - H46A = 120.0
C41A - C46A - H46A = 120.0
C56A - C51A - C52A = 118.9(8)
C56A - C51A - C17 = 120.5(8)
C52A - C51A - C17 = 120.6(9)
C53A - C52A - C51A = 119.7(11)
C53A - C52A - H52A = 120.2
C51A - C52A - H52A = 120.2
C54A - C53A - C52A = 121.2(10)
C54A - C53A - H53A = 119.4
C52A - C53A - H53A = 119.4
C53A - C54A - C55A = 121.4(10)
C53A - C54A - H54A = 119.3
C55A - C54A - H54A = 119.3
C54A - C55A - C56A = 117.4(11)
C54A - C55A - H55A = 121.3
C56A - C55A - H55A = 121.3
C51A - C56A - C55A = 121.3(9)
C51A - C56A - C57A = 126.1(11)
C55A - C56A - C57A = 111.0(12)
N61A - C57A - C58A = 105.5(17)
N61A - C57A - C56A = 127.8(14)
C58A - C57A - C56A = 126.4(17)
N59A - C58A - C57A = 109.3(18)
N59A - C58A - H58A = 125.3
C57A - C58A - H58A = 125.3
C62A - N59A - C58A = 138(3)
C62A - N59A - N60A = 115(3)
C58A - N59A - N60A = 106.3(17)

N61A - N60A - N59A = 105.7(14)
N60A - N61A - C57A = 113.1(16)
N59A - C62A - C63A = 117(3)
N59A - C62A - N67A = 123(3)
C63A - C62A - N67A = 120.0
C62A - C63A - C64A = 120.0
C62A - C63A - H63A = 120.0
C64A - C63A - H63A = 120.0
C65A - C64A - C63A = 120.0
C65A - C64A - H64A = 120.0
C63A - C64A - H64A = 120.0
C64A - C65A - C66A = 120.0
C64A - C65A - H65A = 120.0
C66A - C65A - H65A = 120.0
C65A - C66A - N67A = 120.0
C65A - C66A - H66A = 120.0
N67A - C66A - H66A = 120.0
C66A - N67A - C62A = 120.0
N61B - C57B - C58B = 105.5(17)
N59B - C58B - C57B = 109.3(18)
N59B - C58B - H58B = 125.3
C57B - C58B - H58B = 125.3
C58B - N59B - C62B = 134(2)
C58B - N59B - N60B = 106.3(17)
C62B - N59B - N60B = 119(2)
N61B - N60B - N59B = 105.7(14)
N60B - N61B - C57B = 113.1(16)
C63B - C62B - N67B = 120.0
C63B - C62B - N59B = 109(2)
N67B - C62B - N59B = 131(2)
C64B - C63B - C62B = 120.0
C64B - C63B - H63B = 120.0
C62B - C63B - H63B = 120.0
C65B - C64B - C63B = 120.0
C65B - C64B - H64B = 120.0
C63B - C64B - H64B = 120.0
C66B - C65B - C64B = 120.0
C66B - C65B - H65B = 120.0
C64B - C65B - H65B = 120.0
C65B - C66B - N67B = 120.0
C65B - C66B - H66B = 120.0
N67B - C66B - H66B = 120.0
C66B - N67B - C62B = 120.0
C42B - C41B - C46B = 120.0

C42B - C41B - C12 = 117.6(6)
C46B - C41B - C12 = 122.2(6)
C41B - C42B - C43B = 120.0
C41B - C42B - H42B = 120.0
C43B - C42B - H42B = 120.0
C44B - C43B - C42B = 120.0
C44B - C43B - H43B = 120.0
C42B - C43B - H43B = 120.0
C45B - C44B - C43B = 120.0
C45B - C44B - H44B = 120.0
C43B - C44B - H44B = 120.0
C44B - C45B - C46B = 120.0
C44B - C45B - H45B = 120.0
C46B - C45B - H45B = 120.0
C81 - C46B - C45B = 112.5(13)
C81 - C46B - C41B = 123.4(13)
C45B - C46B - C41B = 120.0
C56B - C51B - C52B = 118.9(8)
C56B - C51B - C17 = 120.5(8)
C52B - C51B - C17 = 120.6(9)
C53B - C52B - C51B = 119.7(11)
C53B - C52B - H52B = 120.2
C51B - C52B - H52B = 120.2
C54B - C53B - C52B = 121.2(10)
C54B - C53B - H53B = 119.4
C52B - C53B - H53B = 119.4
C53B - C54B - C55B = 121.4(10)
C53B - C54B - H54B = 119.3
C55B - C54B - H54B = 119.3
C54B - C55B - C56B = 117.4(11)
C54B - C55B - H55B = 121.3
C56B - C55B - H55B = 121.3
C51B - C56B - C55B = 121.3(9)
C51B - C56B - H56B = 119.3
C55B - C56B - H56B = 119.3
C85 - C81 - N82 = 117(4)
C85 - C81 - C46B = 126(3)
N82 - C81 - C46B = 117(2)
N83 - N82 - C81 = 103(2)
N82 - N83 - N84 = 112(3)
C86 - N84 - N83 = 129(4)
C86 - N84 - C85 = 127(3)
N83 - N84 - C85 = 103(3)
C81 - C85 - N84 = 105(3)

C81 - C85 - H85 = 127.4
N84 - C85 - H85 = 127.4
C91 - C86 - N84 = 125(5)
C91 - C86 - N87 = 121(4)
N84 - C86 - N87 = 114(3)
C88 - N87 - C86 = 114(3)
C89 - C88 - N87 = 118(4)
C89 - C88 - H88 = 120.9
N87 - C88 - H88 = 120.9
C88 - C89 - C90 = 121(4)
C88 - C89 - H89 = 119.6
C90 - C89 - H89 = 119.6
C91 - C90 - C89 = 114(4)
C91 - C90 - H90 = 123.2
C89 - C90 - H90 = 123.2
C86 - C91 - C90 = 132(5)
C86 - C91 - H91 = 114.2
C90 - C91 - H91 = 114.2
C75 - N71 - C72 = 104.4(12)
C75 - N71 - Zn1 = 129.0(10)
C72 - N71 - Zn1 = 126.6(8)
C73 - C72 - N71 = 107.4(17)
C73 - C72 - H72 = 126.3
N71 - C72 - H72 = 126.3
N74 - C73 - C72 = 108.2(18)
N74 - C73 - H73 = 125.9
C72 - C73 - H73 = 125.9
C73 - N74 - C75 = 109.5(15)
C73 - N74 - C76 = 126.7(15)
C75 - N74 - C76 = 123.7(17)
N71 - C75 - N74 = 110.3(17)
N71 - C75 - H75 = 124.8
N74 - C75 - H75 = 124.8
N74 - C76 - H76A = 109.5
N74 - C76 - H76B = 109.5
H76A - C76 - H76B = 109.5
N74 - C76 - H76C = 109.5
H76A - C76 - H76C = 109.5
H76B - C76 - H76C = 109.5

9.7. Torsion angles [°].

C18 - N1 - C1 - C2 = -177.9(10)
Zn1 - N1 - C1 - C2 = 12.9(14)
C18 - N1 - C1 - C20 = 0.3(11)

Zn1 - N1 - C1 - C20 = -168.9(6)
 N1 - C1 - C2 - C3 = -2.3(17)
 C20 - C1 - C2 - C3 = 179.8(10)
 N1 - C1 - C2 - C21 = 175.5(8)
 C20 - C1 - C2 - C21 = -2.3(15)
 C6 - N2 - C3 - C2 = -175.5(10)
 Zn1 - N2 - C3 - C2 = -1.3(14)
 C6 - N2 - C3 - C4 = 3.4(11)
 Zn1 - N2 - C3 - C4 = 177.6(6)
 C1 - C2 - C3 - N2 = -4.0(17)
 C21 - C2 - C3 - N2 = 178.3(9)
 C1 - C2 - C3 - C4 = 177.3(10)
 C21 - C2 - C3 - C4 = -0.4(15)
 N2 - C3 - C4 - C5 = -2.3(12)
 C2 - C3 - C4 - C5 = 176.6(10)
 C3 - C4 - C5 - C6 = 0.2(11)
 C3 - N2 - C6 - C7 = 179.0(10)
 Zn1 - N2 - C6 - C7 = 4.8(14)
 C3 - N2 - C6 - C5 = -3.3(11)
 Zn1 - N2 - C6 - C5 = -177.5(6)
 C4 - C5 - C6 - N2 = 1.9(11)
 C4 - C5 - C6 - C7 = 179.6(10)
 N2 - C6 - C7 - C8 = 7.3(17)
 C5 - C6 - C7 - C8 = -170.1(10)
 N2 - C6 - C7 - C31 = -171.4(9)
 C5 - C6 - C7 - C31 = 11.2(15)
 C11 - N3 - C8 - C7 = 175.7(10)
 Zn1 - N3 - C8 - C7 = -22.0(15)
 C11 - N3 - C8 - C9 = -1.8(12)
 Zn1 - N3 - C8 - C9 = 160.4(7)
 C6 - C7 - C8 - N3 = 2.1(17)
 C31 - C7 - C8 - N3 = -179.2(9)
 C6 - C7 - C8 - C9 = 179.3(10)
 C31 - C7 - C8 - C9 = -2.1(15)
 N3 - C8 - C9 - C10 = 1.8(12)
 C7 - C8 - C9 - C10 = -175.8(10)
 C8 - C9 - C10 - C11 = -1.0(12)
 C8 - N3 - C11 - C12 = -178.0(10)
 Zn1 - N3 - C11 - C12 = 19.5(15)
 C8 - N3 - C11 - C10 = 1.2(11)
 Zn1 - N3 - C11 - C10 = -161.3(6)
 C9 - C10 - C11 - N3 = -0.1(12)
 C9 - C10 - C11 - C12 = 179.2(10)
 N3 - C11 - C12 - C13 = -4.3(18)

C10 - C11 - C12 - C13 = 176.6(10)
 N3 - C11 - C12 - C41A = 174.9(9)
 C10 - C11 - C12 - C41A = -4.2(15)
 N3 - C11 - C12 - C41B = 174.9(9)
 C10 - C11 - C12 - C41B = -4.2(15)
 C16 - N4 - C13 - C12 = -174.4(9)
 Zn1 - N4 - C13 - C12 = 0.5(14)
 C16 - N4 - C13 - C14 = 0.5(11)
 Zn1 - N4 - C13 - C14 = 175.4(6)
 C11 - C12 - C13 - N4 = -6.7(17)
 C41A - C12 - C13 - N4 = 174.1(8)
 C41B - C12 - C13 - N4 = 174.1(8)
 C11 - C12 - C13 - C14 = 179.4(10)
 C41A - C12 - C13 - C14 = 0.2(15)
 C41B - C12 - C13 - C14 = 0.2(15)
 N4 - C13 - C14 - C15 = -0.8(12)
 C12 - C13 - C14 - C15 = 173.7(10)
 C13 - C14 - C15 - C16 = 0.8(11)
 C13 - N4 - C16 - C17 = 175.6(9)
 Zn1 - N4 - C16 - C17 = 0.6(14)
 C13 - N4 - C16 - C15 = 0.0(11)
 Zn1 - N4 - C16 - C15 = -174.9(6)
 C14 - C15 - C16 - N4 = -0.5(12)
 C14 - C15 - C16 - C17 = -176.1(9)
 N4 - C16 - C17 - C18 = 12.8(16)
 C15 - C16 - C17 - C18 = -172.2(10)
 N4 - C16 - C17 - C51B = -167.0(9)
 C15 - C16 - C17 - C51B = 7.9(15)
 N4 - C16 - C17 - C51A = -167.0(9)
 C15 - C16 - C17 - C51A = 7.9(15)
 C1 - N1 - C18 - C17 = 173.4(10)
 Zn1 - N1 - C18 - C17 = -17.4(14)
 C1 - N1 - C18 - C19 = -1.9(11)
 Zn1 - N1 - C18 - C19 = 167.3(6)
 C16 - C17 - C18 - N1 = -3.8(17)
 C51B - C17 - C18 - N1 = 176.1(9)
 C51A - C17 - C18 - N1 = 176.1(9)
 C16 - C17 - C18 - C19 = 170.9(9)
 C51B - C17 - C18 - C19 = -9.2(15)
 C51A - C17 - C18 - C19 = -9.2(15)
 N1 - C18 - C19 - C20 = 3.0(11)
 C17 - C18 - C19 - C20 = -172.5(10)
 C18 - C19 - C20 - C1 = -2.7(11)
 N1 - C1 - C20 - C19 = 1.6(11)

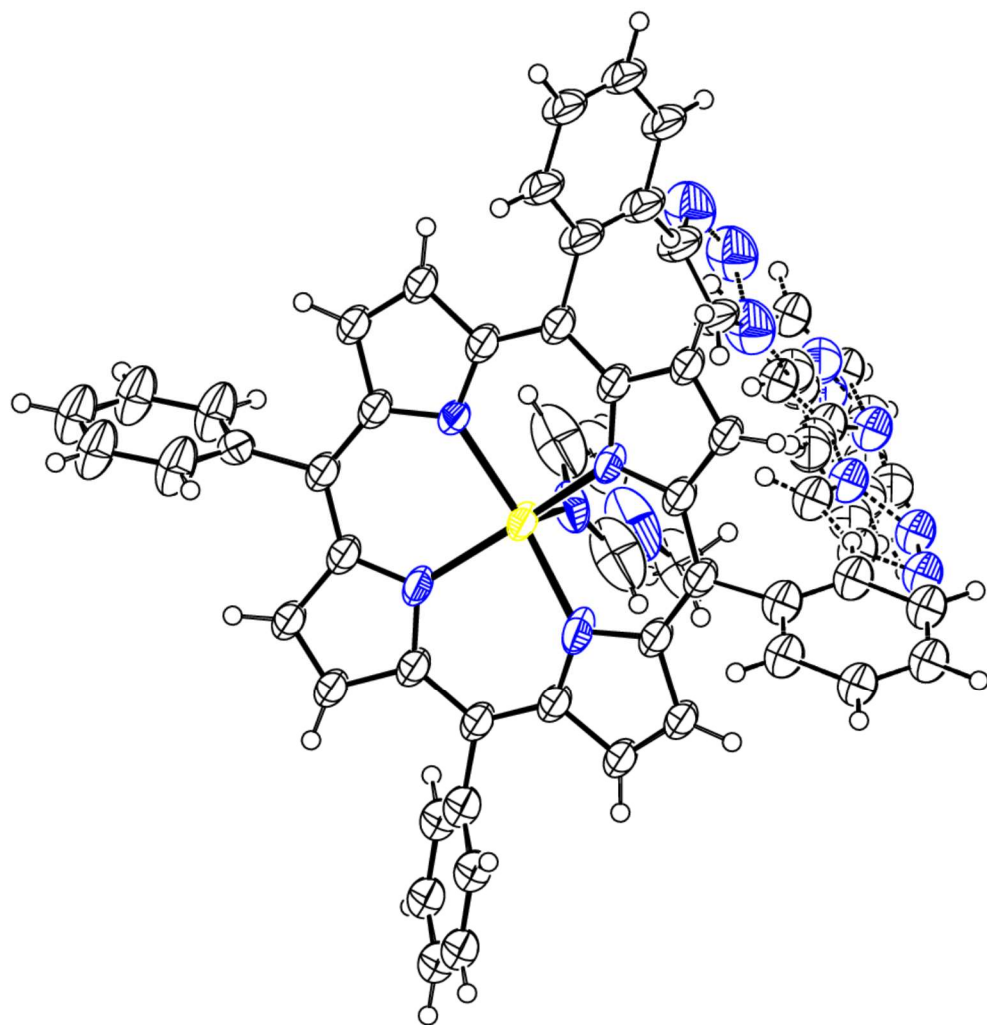
C2 - C1 - C20 - C19 = 179.8(10)
 C1 - C2 - C21 - C22 = 76.3(10)
 C3 - C2 - C21 - C22 = -105.7(9)
 C1 - C2 - C21 - C26 = -108.2(9)
 C3 - C2 - C21 - C26 = 69.7(10)
 C26 - C21 - C22 - C23 = 0.0
 C2 - C21 - C22 - C23 = 175.4(7)
 C21 - C22 - C23 - C24 = 0.0
 C22 - C23 - C24 - C25 = 0.0
 C23 - C24 - C25 - C26 = 0.0
 C24 - C25 - C26 - C21 = 0.0
 C22 - C21 - C26 - C25 = 0.0
 C2 - C21 - C26 - C25 = -175.5(7)
 C8 - C7 - C31 - C32 = -119.3(8)
 C6 - C7 - C31 - C32 = 59.4(10)
 C8 - C7 - C31 - C36 = 59.1(10)
 C6 - C7 - C31 - C36 = -122.1(8)
 C36 - C31 - C32 - C33 = 0.0
 C7 - C31 - C32 - C33 = 178.5(7)
 C31 - C32 - C33 - C34 = 0.0
 C32 - C33 - C34 - C35 = 0.0
 C33 - C34 - C35 - C36 = 0.0
 C34 - C35 - C36 - C31 = 0.0
 C32 - C31 - C36 - C35 = 0.0
 C7 - C31 - C36 - C35 = -178.5(7)
 C11 - C12 - C41A - C42A = -65.8(10)
 C13 - C12 - C41A - C42A = 113.5(9)
 C11 - C12 - C41A - C46A = 109.4(9)
 C13 - C12 - C41A - C46A = -71.3(10)
 C46A - C41A - C42A - C43A = 0.0
 C12 - C41A - C42A - C43A = 175.3(8)
 C41A - C42A - C43A - C44A = 0.0
 C42A - C43A - C44A - C45A = 0.0
 C43A - C44A - C45A - C46A = 0.0
 C44A - C45A - C46A - C41A = 0.0
 C42A - C41A - C46A - C45A = 0.0
 C12 - C41A - C46A - C45A = -175.1(8)
 C18 - C17 - C51A - C56A = -111.1(10)
 C16 - C17 - C51A - C56A = 68.8(12)
 C18 - C17 - C51A - C52A = 68.9(12)
 C16 - C17 - C51A - C52A = -111.2(10)
 C56A - C51A - C52A - C53A = -0.7(15)
 C17 - C51A - C52A - C53A = 179.4(9)
 C51A - C52A - C53A - C54A = 0.5(17)

C52A - C53A - C54A - C55A = 1.4(18)
 C53A - C54A - C55A - C56A = -3.1(17)
 C52A - C51A - C56A - C55A = -1.1(15)
 C17 - C51A - C56A - C55A = 178.9(9)
 C52A - C51A - C56A - C57A = -165.3(11)
 C17 - C51A - C56A - C57A = 14.6(16)
 C54A - C55A - C56A - C51A = 2.9(16)
 C54A - C55A - C56A - C57A = 169.3(11)
 C51A - C56A - C57A - N61A = 129.1(18)
 C55A - C56A - C57A - N61A = -37(2)
 C51A - C56A - C57A - C58A = -59(2)
 C55A - C56A - C57A - C58A = 135.5(17)
 N61A - C57A - C58A - N59A = 0(2)
 C56A - C57A - C58A - N59A = -173.0(16)
 C57A - C58A - N59A - C62A = 172(4)
 C57A - C58A - N59A - N60A = 1(2)
 C62A - N59A - N60A - N61A = -175(3)
 C58A - N59A - N60A - N61A = -2(2)
 N59A - N60A - N61A - C57A = 2(2)
 C58A - C57A - N61A - N60A = -2(2)
 C56A - C57A - N61A - N60A = 171.7(16)
 C58A - N59A - C62A - C63A = 4(4)
 N60A - N59A - C62A - C63A = 174.6(15)
 C58A - N59A - C62A - N67A = -176(2)
 N60A - N59A - C62A - N67A = -6(4)
 N59A - C62A - C63A - C64A = 180(3)
 N67A - C62A - C63A - C64A = 0.0
 C62A - C63A - C64A - C65A = 0.0
 C63A - C64A - C65A - C66A = 0.0
 C64A - C65A - C66A - N67A = 0.0
 C65A - C66A - N67A - C62A = 0.0
 N59A - C62A - N67A - C66A = -180(4)
 C63A - C62A - N67A - C66A = 0.0
 N61B - C57B - C58B - N59B = 0(2)
 C57B - C58B - N59B - C62B = 175(3)
 C57B - C58B - N59B - N60B = 1(2)
 C58B - N59B - N60B - N61B = -2(2)
 C62B - N59B - N60B - N61B = -177(2)
 N59B - N60B - N61B - C57B = 2(2)
 C58B - C57B - N61B - N60B = -2(2)
 C58B - N59B - C62B - C63B = 5(3)
 N60B - N59B - C62B - C63B = 179.2(15)
 C58B - N59B - C62B - N67B = 178.8(19)
 N60B - N59B - C62B - N67B = -7(3)

N67B - C62B - C63B - C64B = 0.0
 N59B - C62B - C63B - C64B = 174(2)
 C62B - C63B - C64B - C65B = 0.0
 C63B - C64B - C65B - C66B = 0.0
 C64B - C65B - C66B - N67B = 0.0
 C65B - C66B - N67B - C62B = 0.0
 C63B - C62B - N67B - C66B = 0.0
 N59B - C62B - N67B - C66B = -173(3)
 C11 - C12 - C41B - C42B = -65.8(10)
 C13 - C12 - C41B - C42B = 113.5(9)
 C11 - C12 - C41B - C46B = 109.4(9)
 C13 - C12 - C41B - C46B = -71.3(10)
 C46B - C41B - C42B - C43B = 0.0
 C12 - C41B - C42B - C43B = 175.3(8)
 C41B - C42B - C43B - C44B = 0.0
 C42B - C43B - C44B - C45B = 0.0
 C43B - C44B - C45B - C46B = 0.0
 C44B - C45B - C46B - C81 = -158.2(16)
 C44B - C45B - C46B - C41B = 0.0
 C42B - C41B - C46B - C81 = 155.7(18)
 C12 - C41B - C46B - C81 = -19.4(18)
 C42B - C41B - C46B - C45B = 0.0
 C12 - C41B - C46B - C45B = -175.1(8)
 C18 - C17 - C51B - C56B = -111.1(10)
 C16 - C17 - C51B - C56B = 68.8(12)
 C18 - C17 - C51B - C52B = 68.9(12)
 C16 - C17 - C51B - C52B = -111.2(10)
 C56B - C51B - C52B - C53B = -0.7(15)
 C17 - C51B - C52B - C53B = 179.4(9)
 C51B - C52B - C53B - C54B = 0.5(17)
 C52B - C53B - C54B - C55B = 1.4(18)
 C53B - C54B - C55B - C56B = -3.1(17)
 C52B - C51B - C56B - C55B = -1.1(15)
 C17 - C51B - C56B - C55B = 178.9(9)
 C54B - C55B - C56B - C51B = 2.9(16)
 C45B - C46B - C81 - C85 = -155(3)
 C41B - C46B - C81 - C85 = 48(4)
 C45B - C46B - C81 - N82 = 16(3)
 C41B - C46B - C81 - N82 = -141(2)
 C85 - C81 - N82 - N83 = -1(4)
 C46B - C81 - N82 - N83 = -173(2)
 C81 - N82 - N83 - N84 = 2(3)
 N82 - N83 - N84 - C86 = 171(3)
 N82 - N83 - N84 - C85 = -2(3)

N82 - C81 - C85 - N84 = 0(4)
C46B - C81 - C85 - N84 = 171(3)
C86 - N84 - C85 - C81 = -172(3)
N83 - N84 - C85 - C81 = 1(4)
N83 - N84 - C86 - C91 = -169(4)
C85 - N84 - C86 - C91 = 2(6)
N83 - N84 - C86 - N87 = 13(5)
C85 - N84 - C86 - N87 = -175(3)
C91 - C86 - N87 - C88 = -2(5)
N84 - C86 - N87 - C88 = 175(3)
C86 - N87 - C88 - C89 = 9(4)
N87 - C88 - C89 - C90 = -11(5)
C88 - C89 - C90 - C91 = 5(5)
N84 - C86 - C91 - C90 = 178(4)
N87 - C86 - C91 - C90 = -5(7)
C89 - C90 - C91 - C86 = 4(7)
C75 - N71 - C72 - C73 = 0.8(14)
Zn1 - N71 - C72 - C73 = -178.1(8)
N71 - C72 - C73 - N74 = 0.4(17)
C72 - C73 - N74 - C75 = -1.4(18)
C72 - C73 - N74 - C76 = 178.4(12)
C72 - N71 - C75 - N74 = -1.6(14)
Zn1 - N71 - C75 - N74 = 177.3(8)
C73 - N74 - C75 - N71 = 2.0(17)
C76 - N74 - C75 - N71 = -177.8(11)

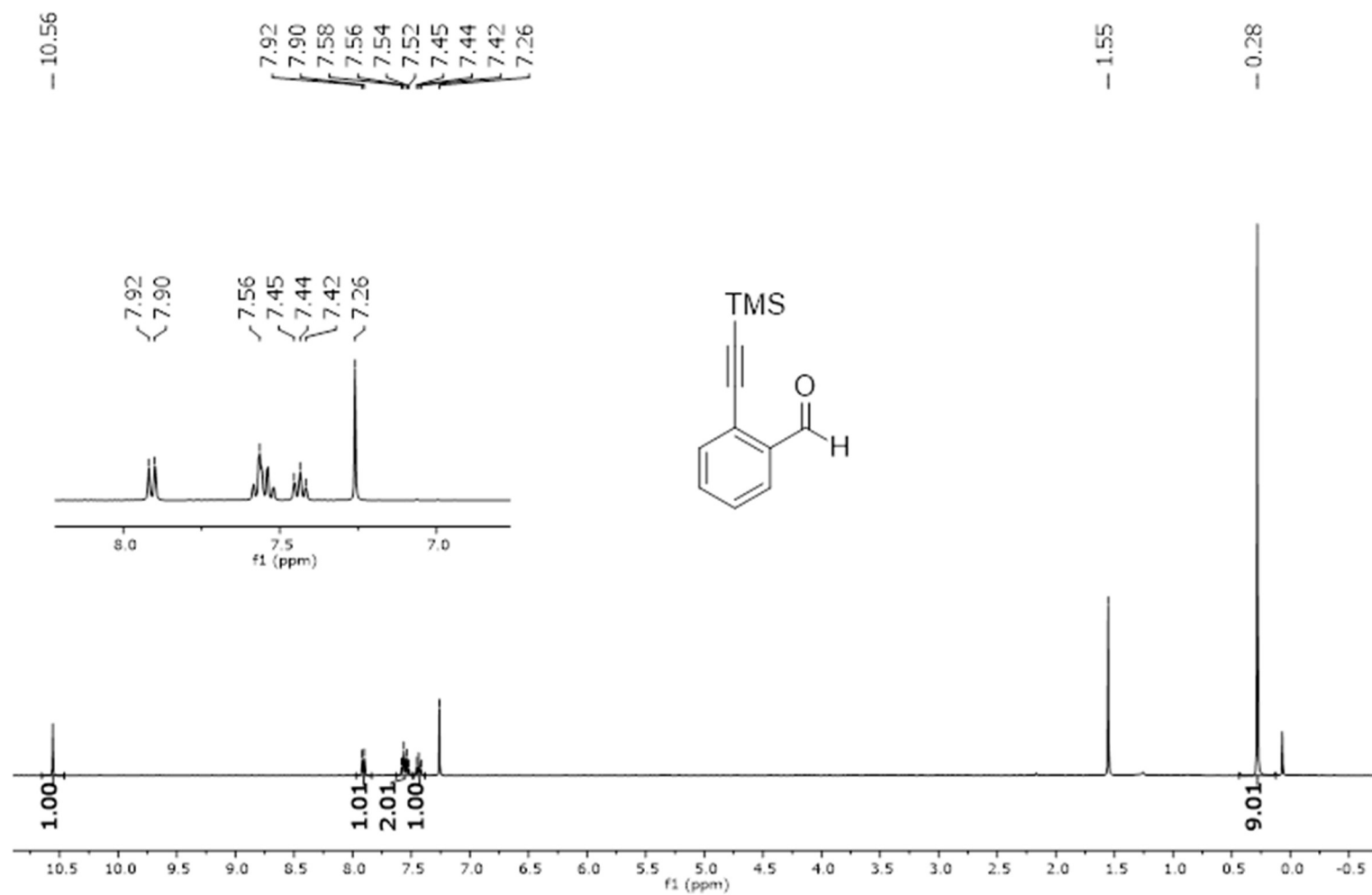
9.8. Structure visualization.



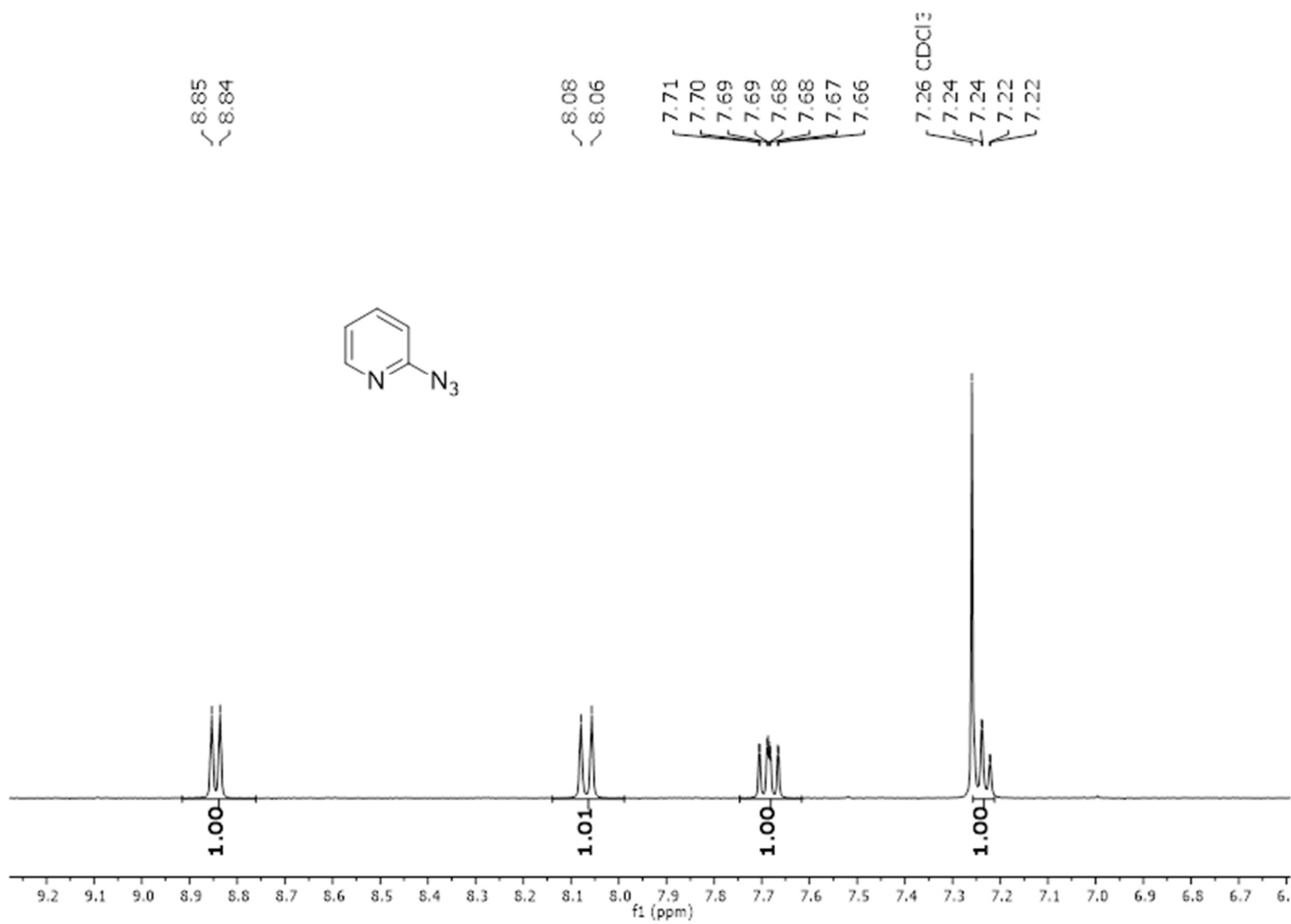
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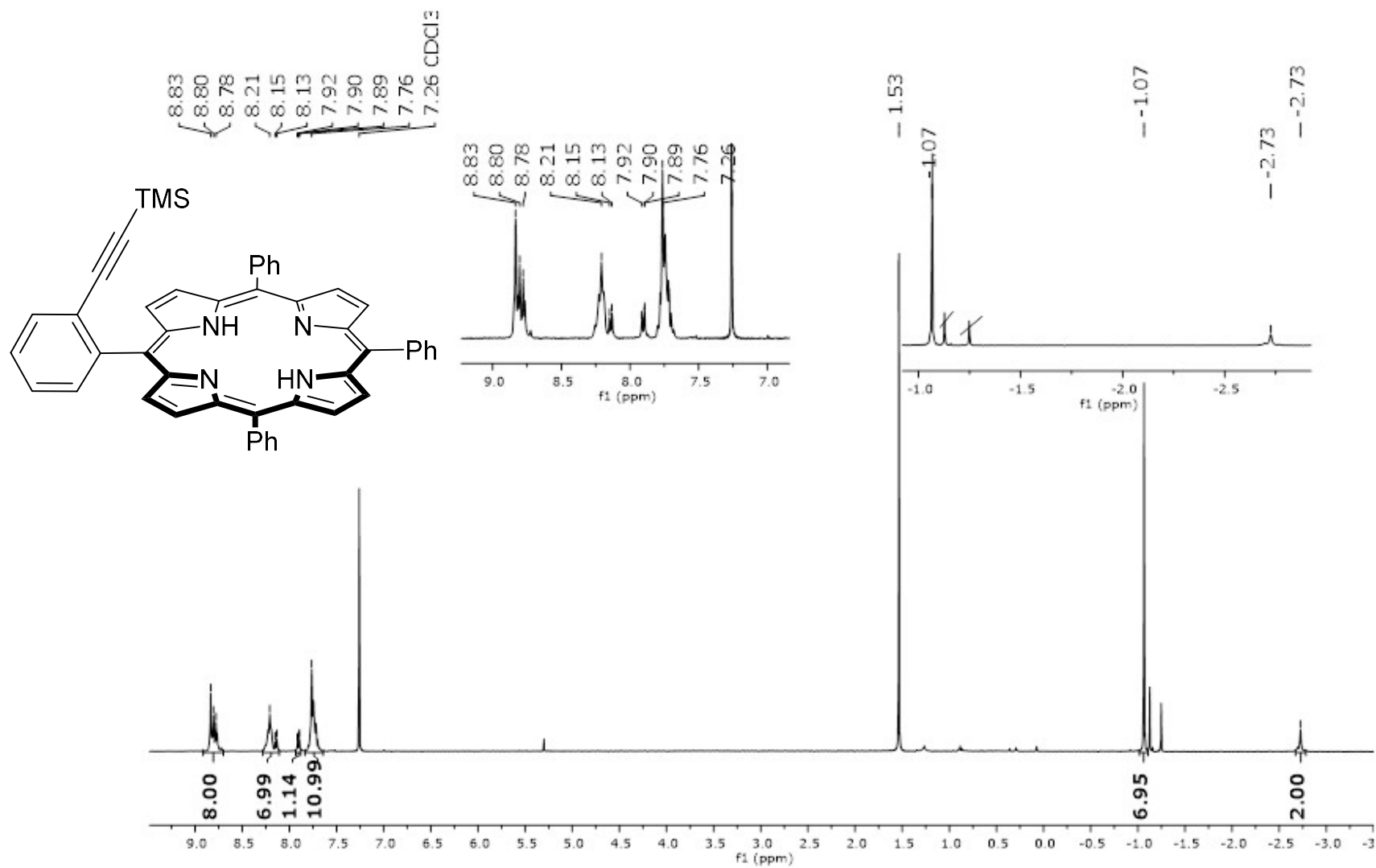
11. NMR spectra.



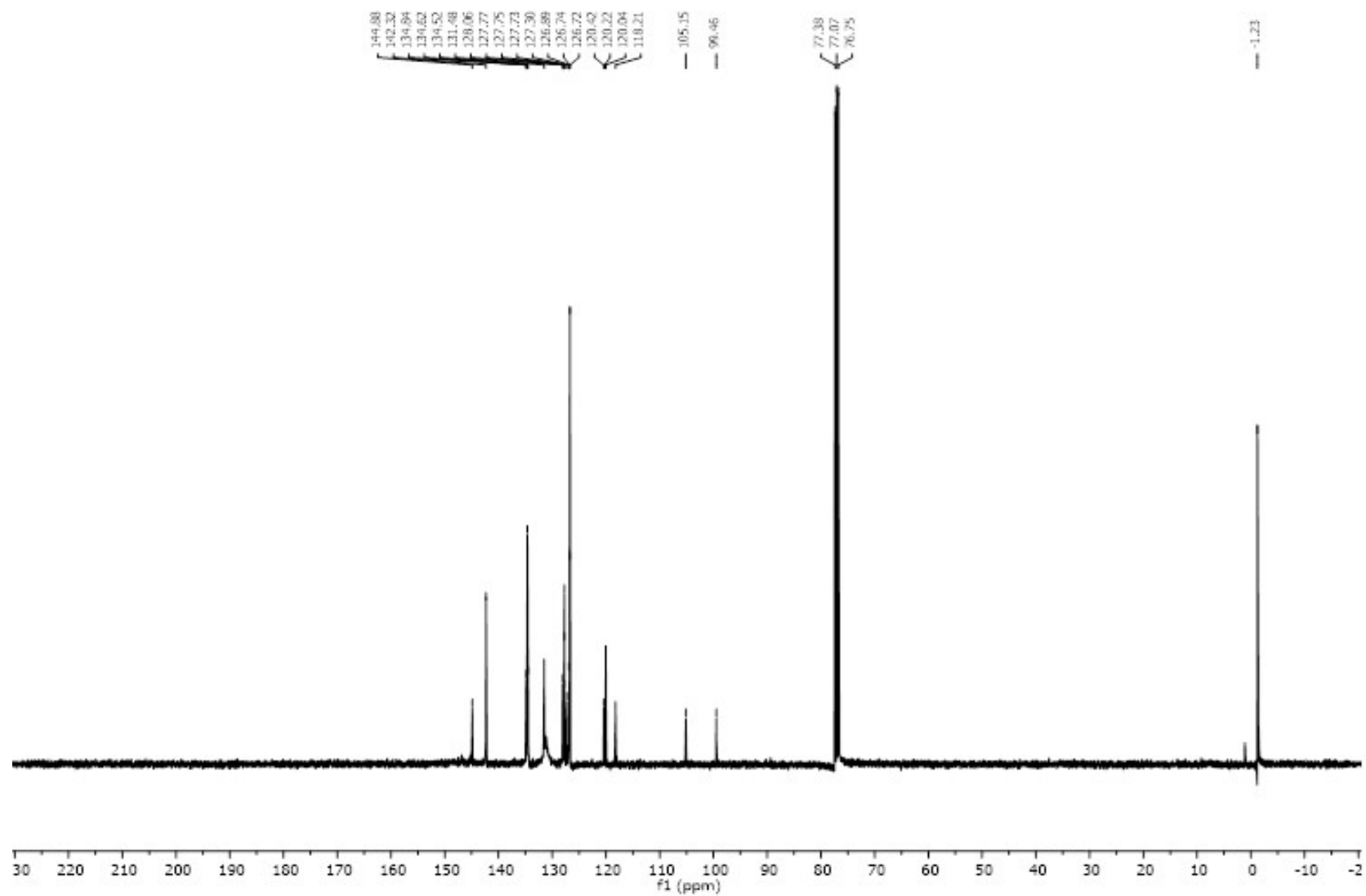
^1H NMR (CDCl_3 , 400 MHz) spectrum of 2-((trimethylsilyl)ethynyl)benzaldehyde.



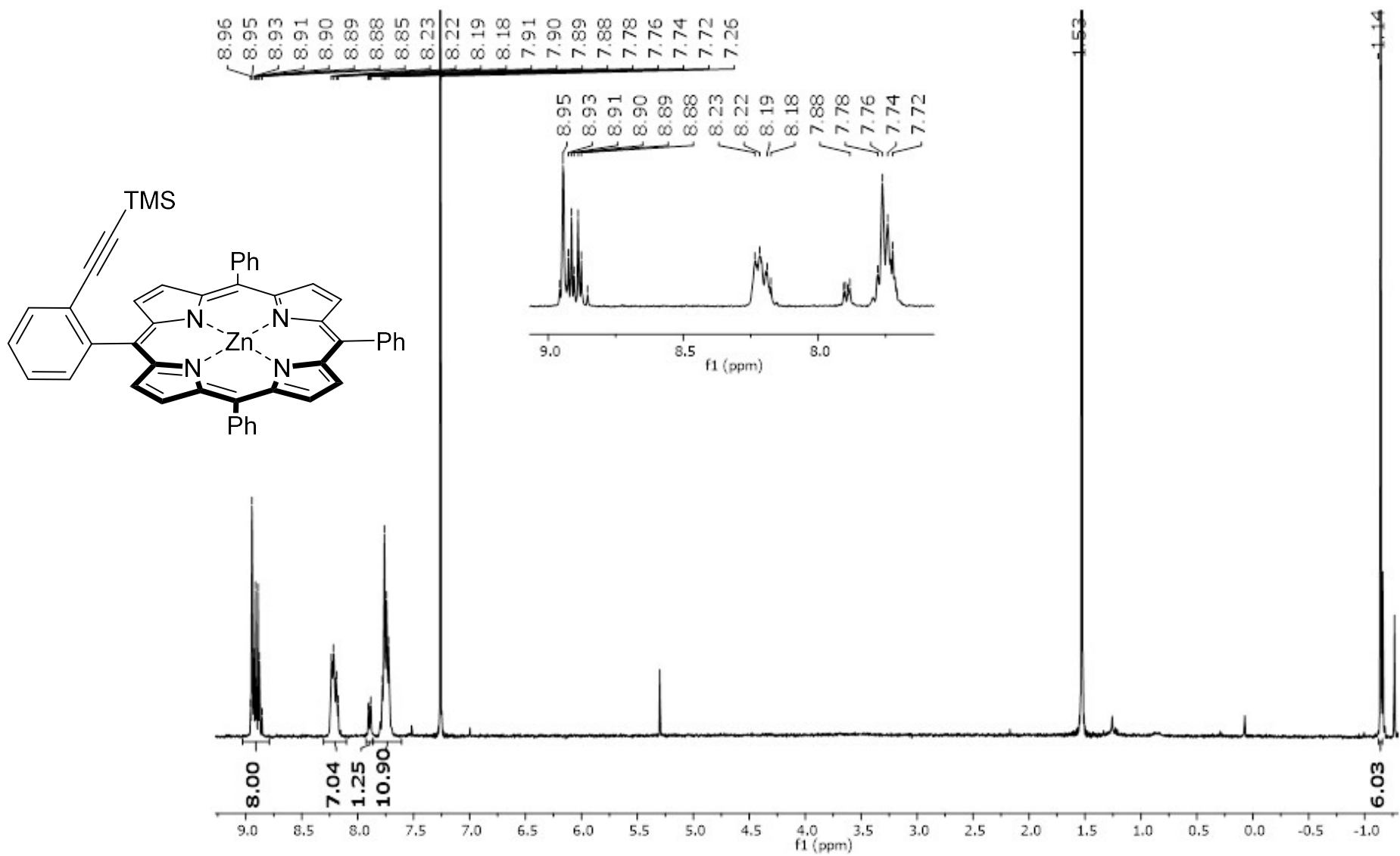
^1H NMR (CDCl₃, 400 MHz) spectrum of 2-azidopyridine.



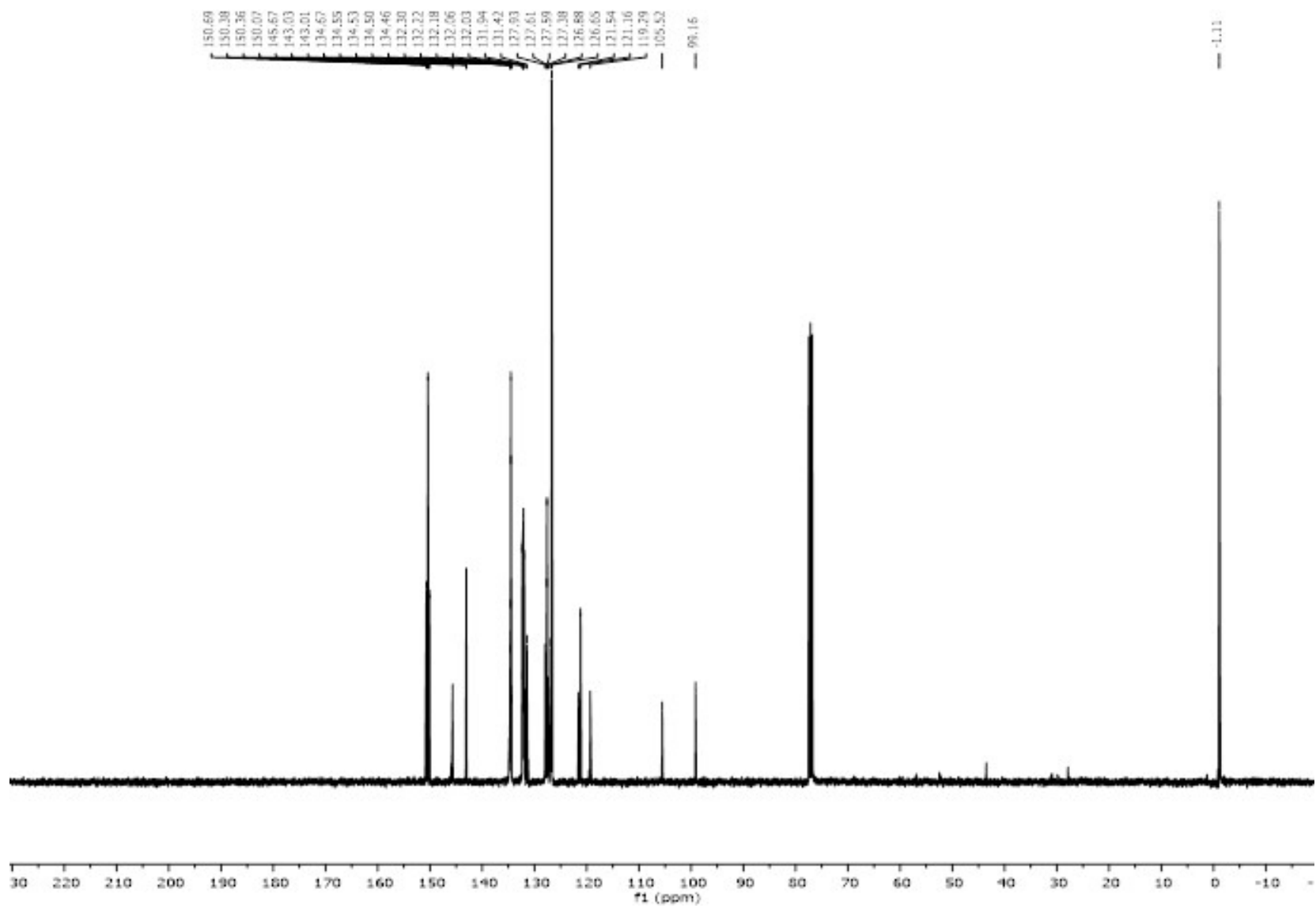
$^1\text{H NMR}$ (CDCl₃, 400 MHz) spectrum of **P1**.



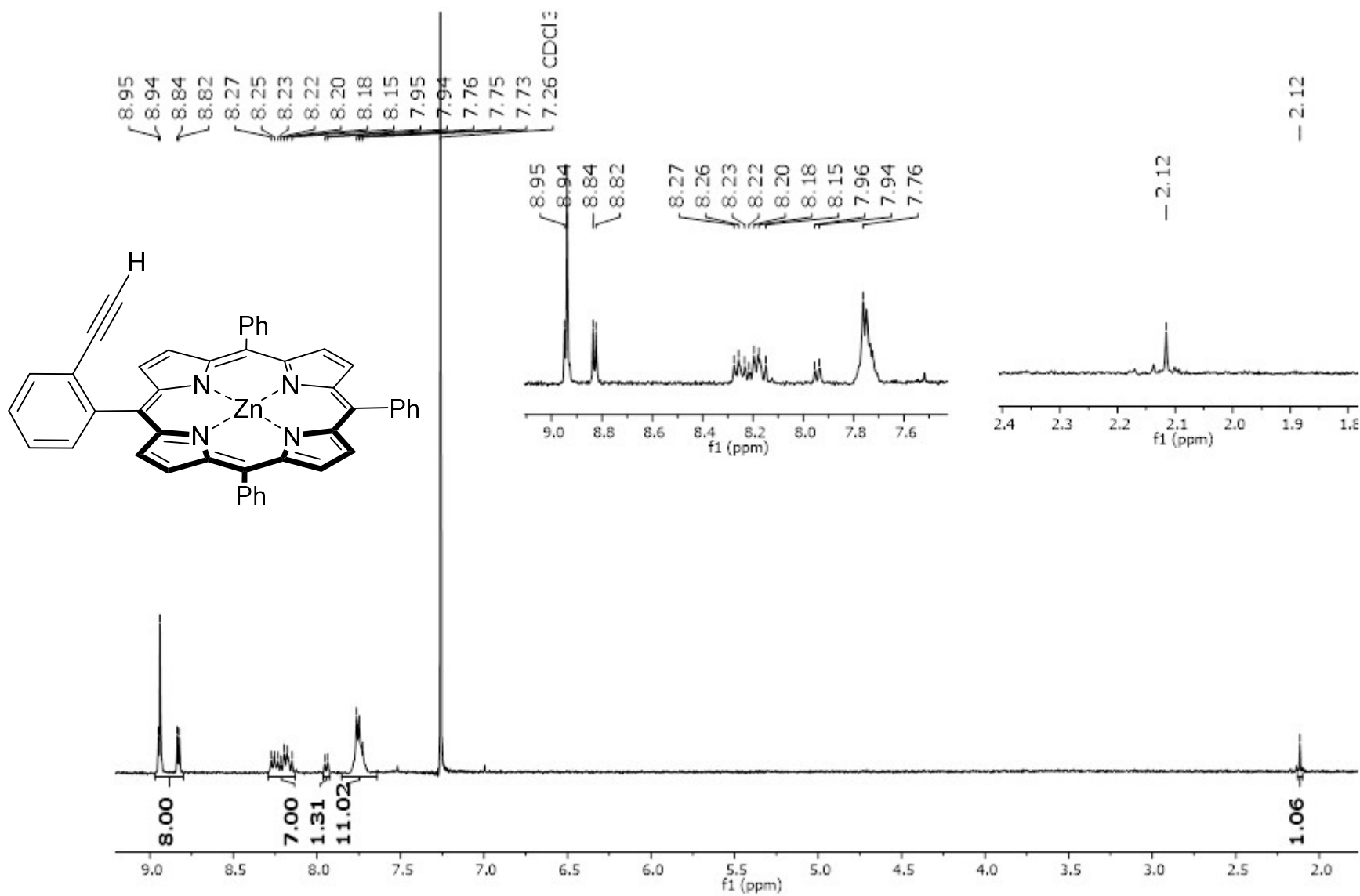
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of **P1**.



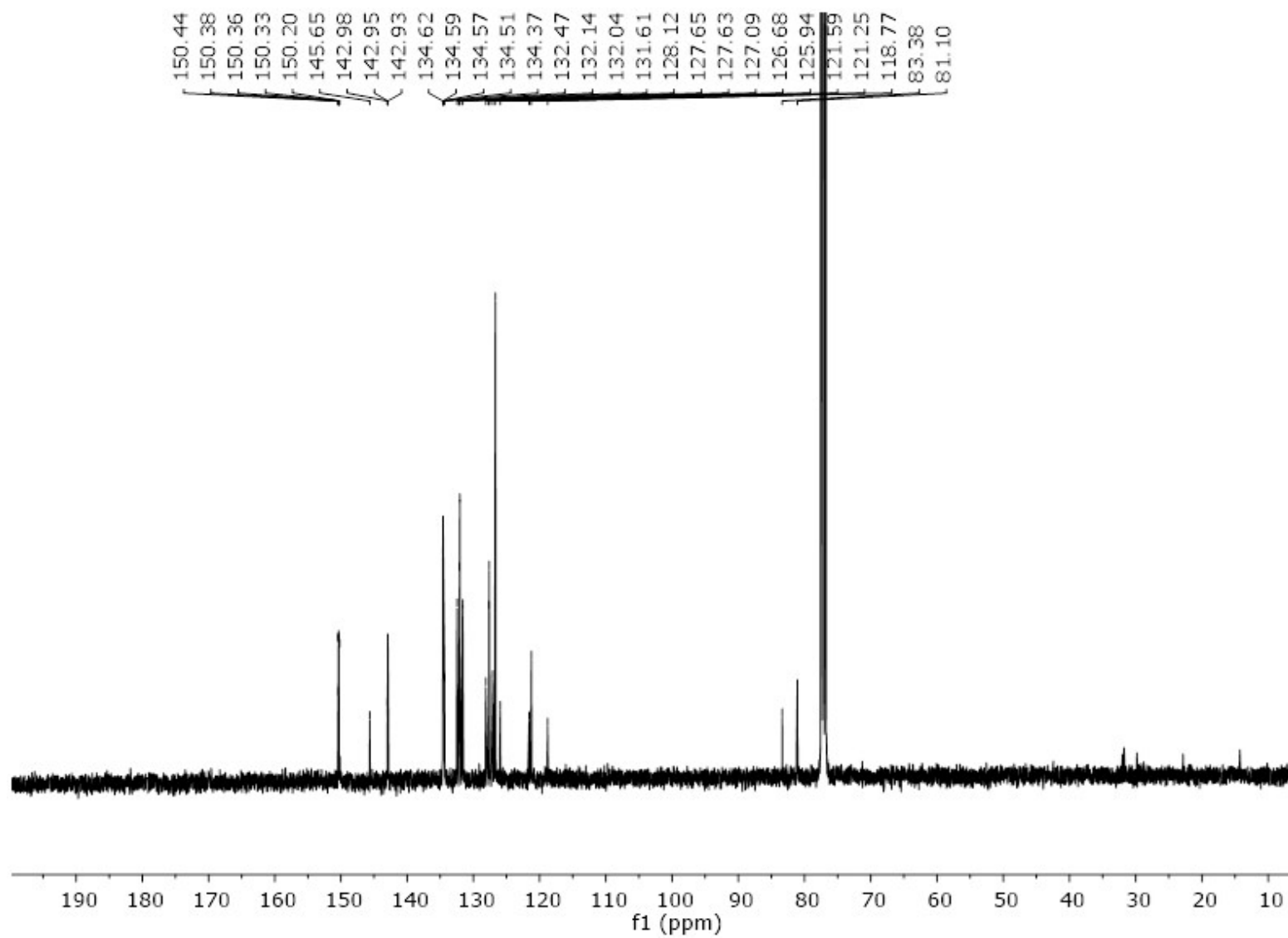
^1H NMR (CDCl₃, 400 MHz) spectrum of **P2**.



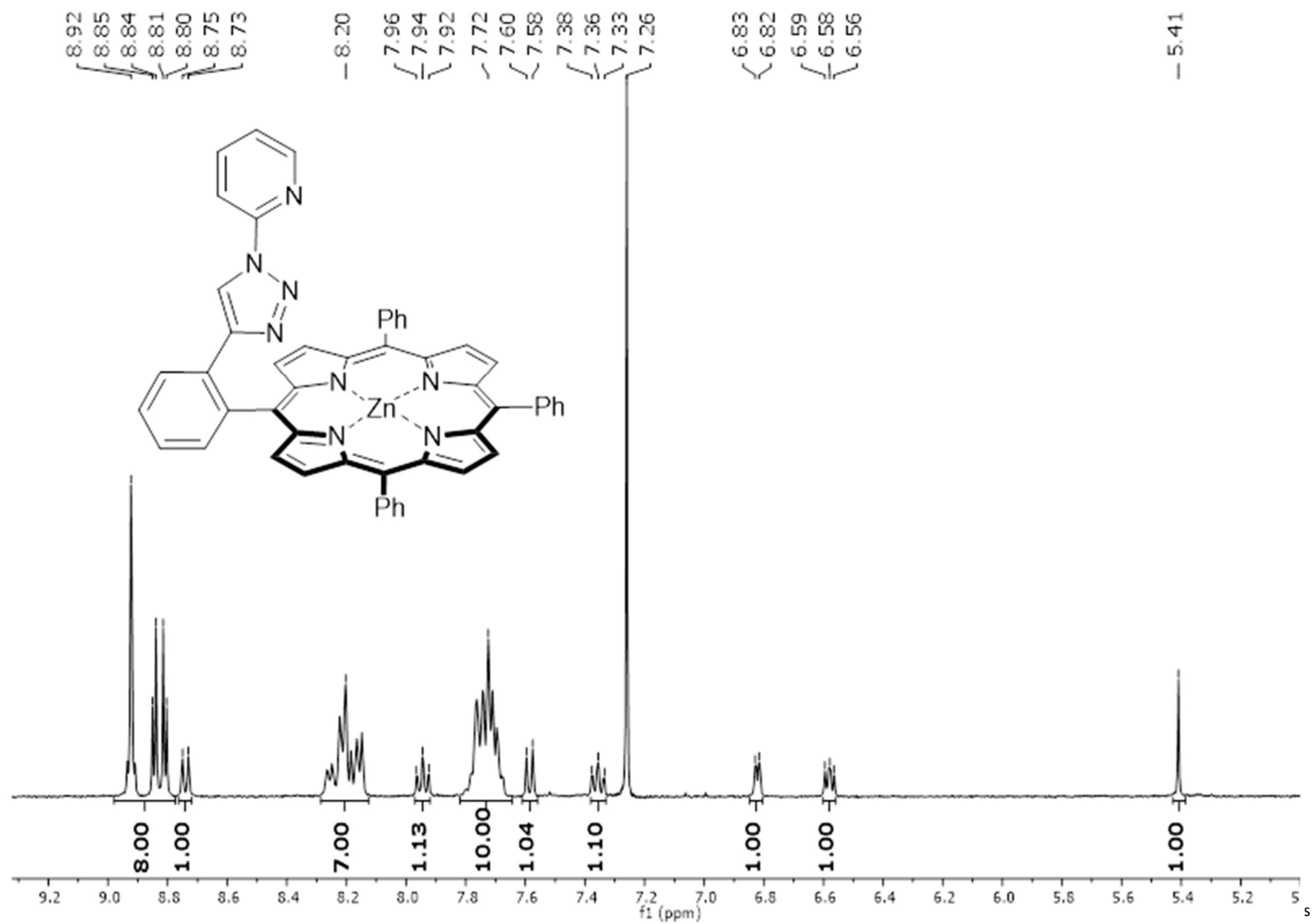
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 101 MHz) of **P2**.



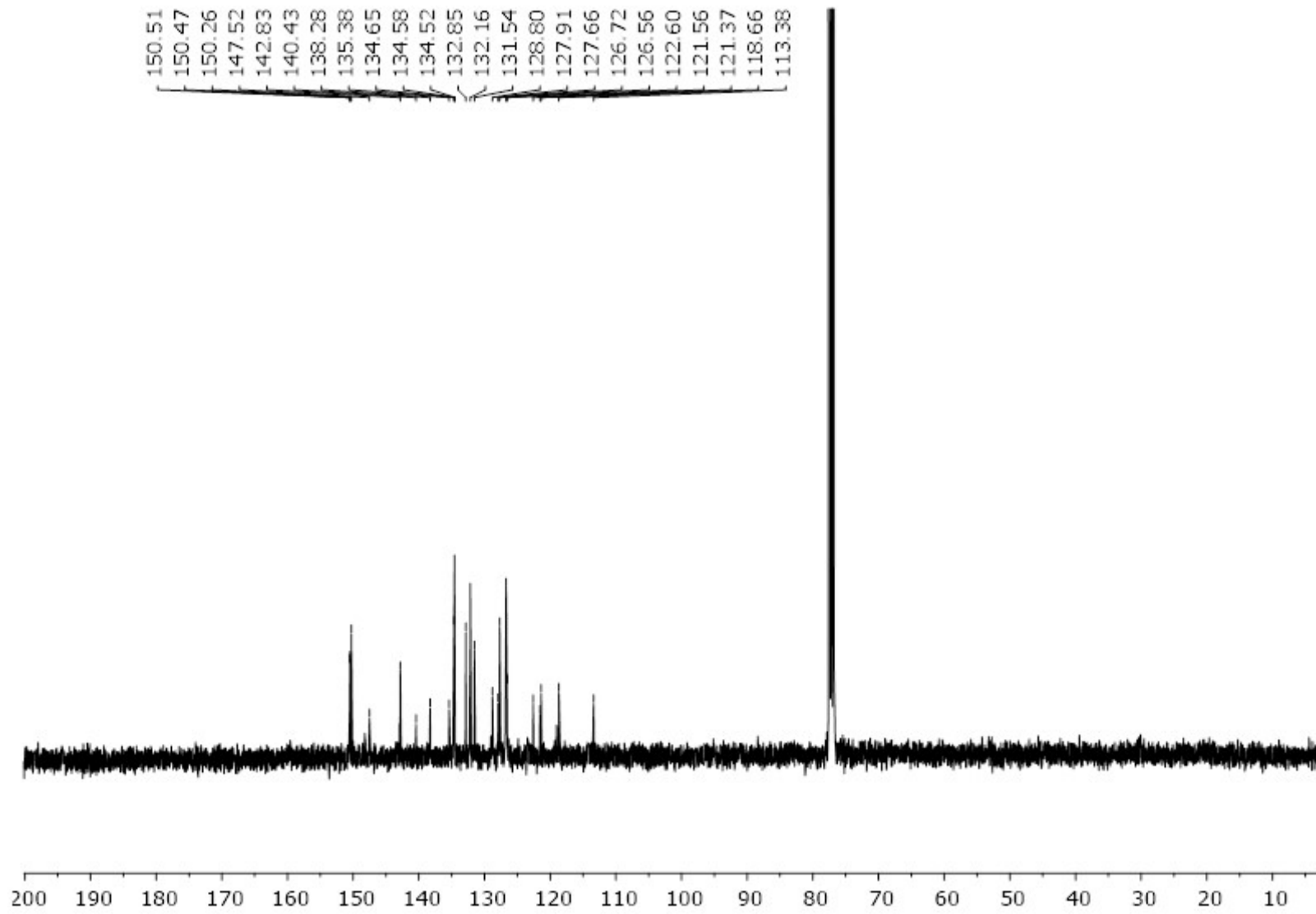
$^1\text{H NMR}$ (CDCl₃, 400 MHz) spectrum of **P3**.



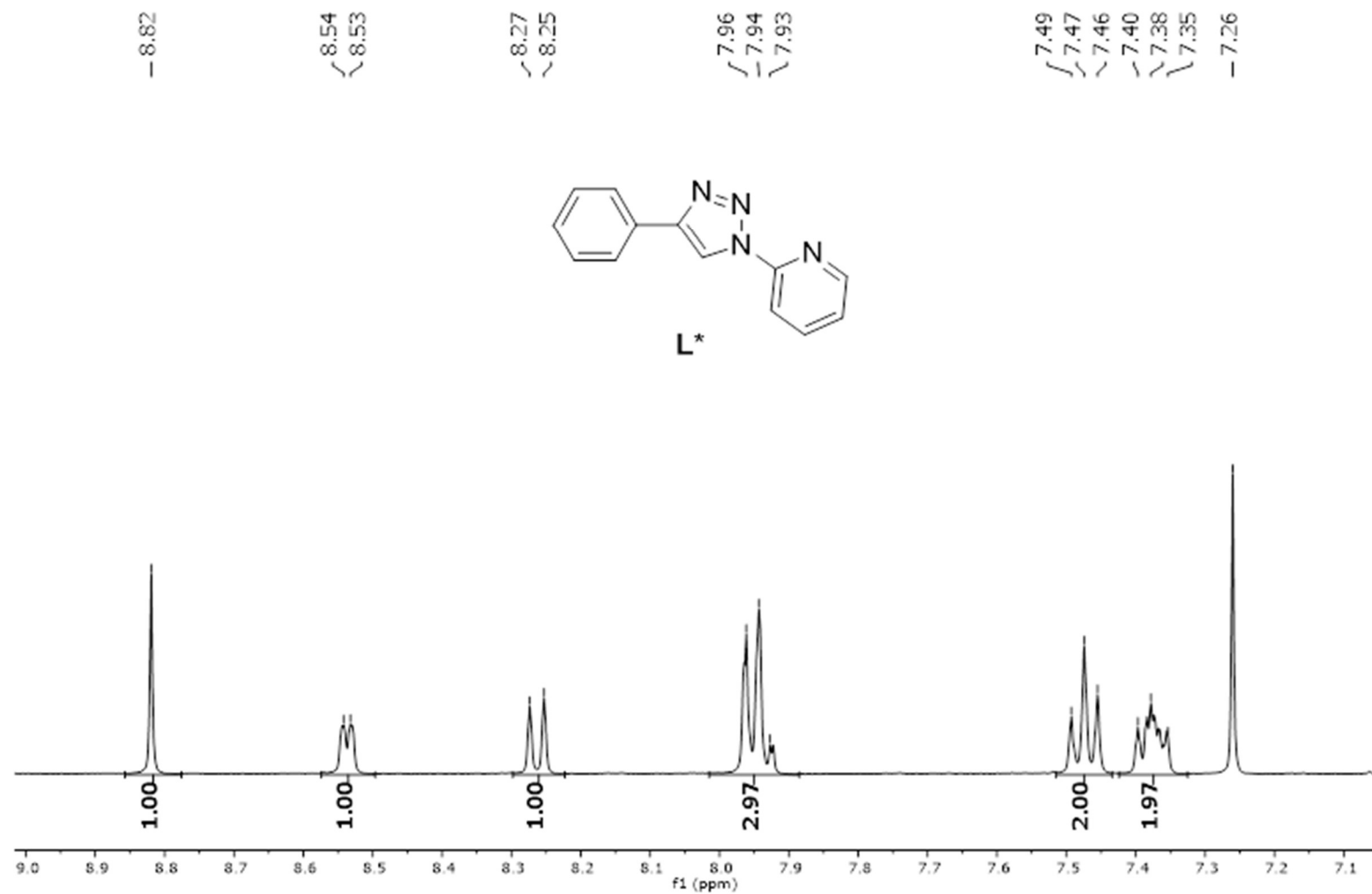
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz) spectrum of **P3**.



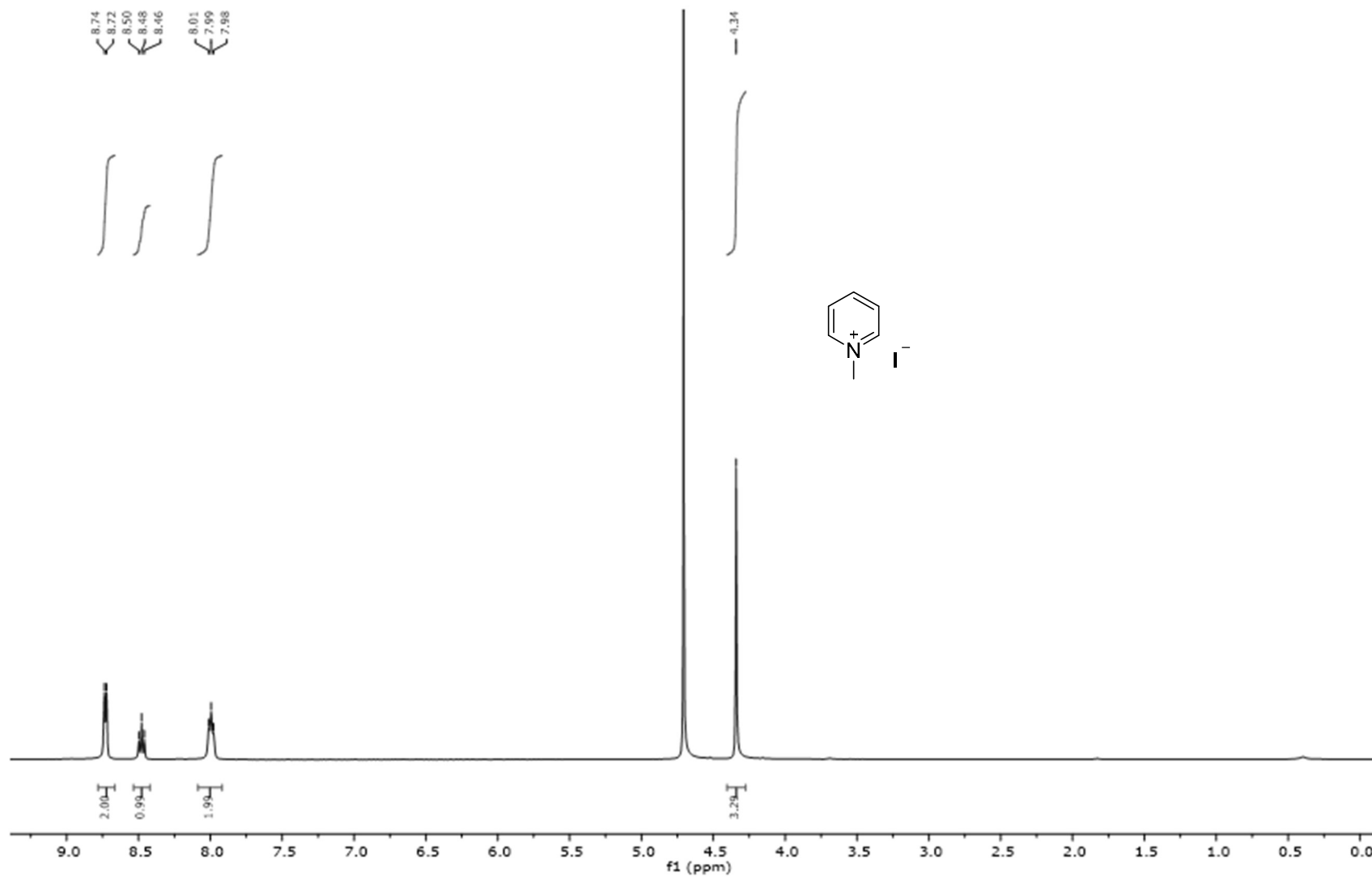
^1H NMR (CDCl₃, 400 MHz) spectrum of L.



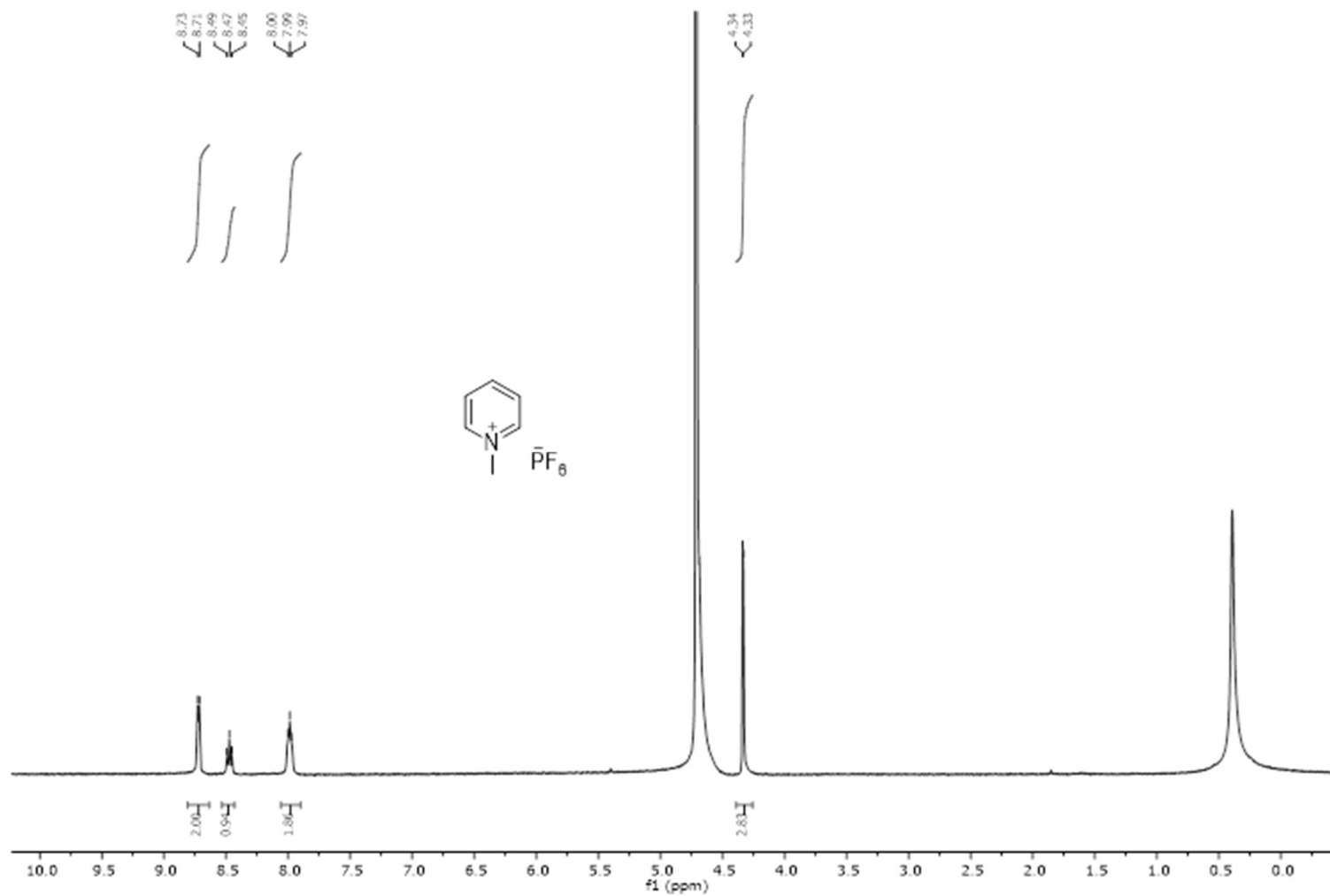
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of L.



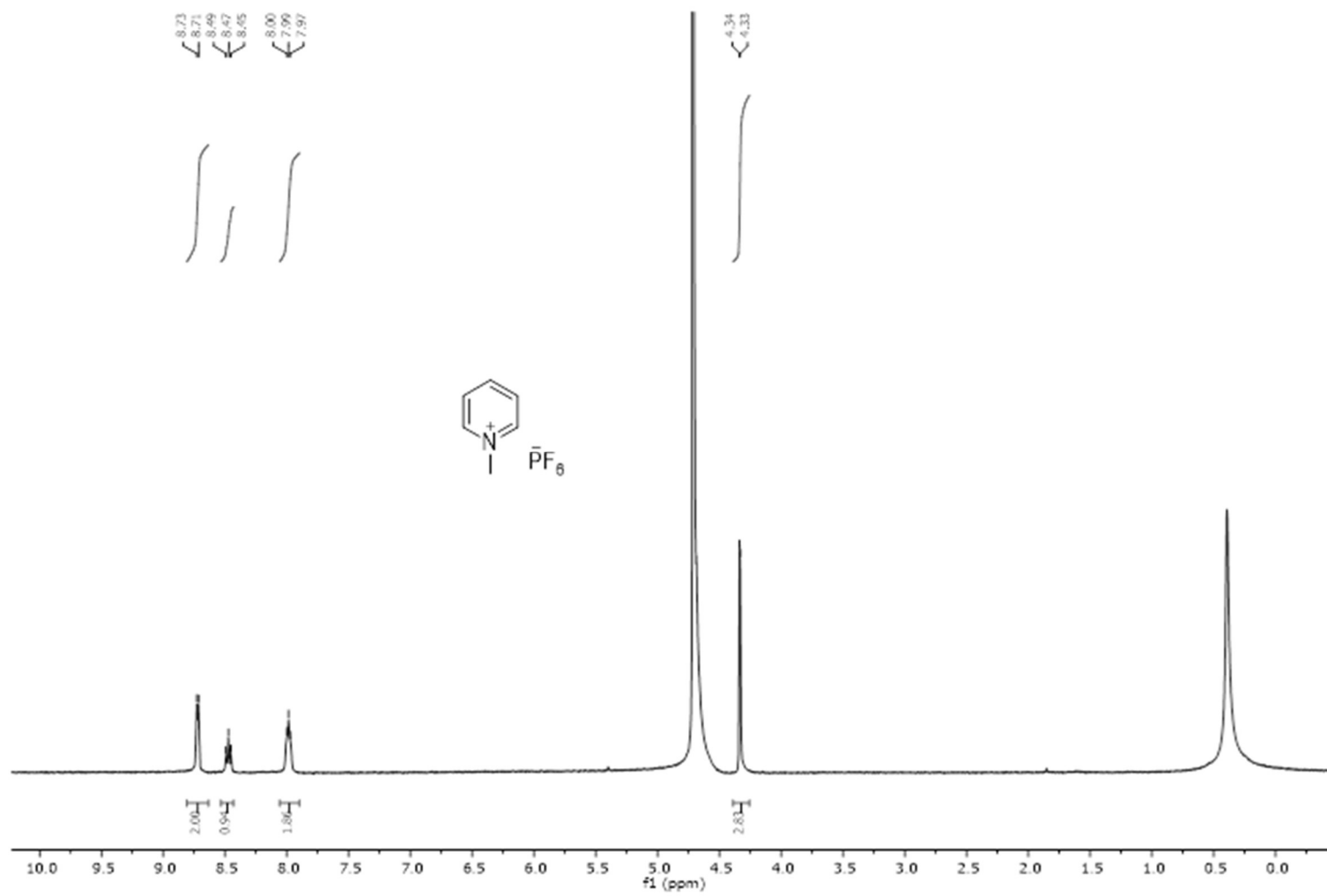
¹H NMR (CDCl₃, 400 MHz) spectrum of 2-(4-phenyl-1H-1,2,3-triazol-1-yl)pyridine (**L***).



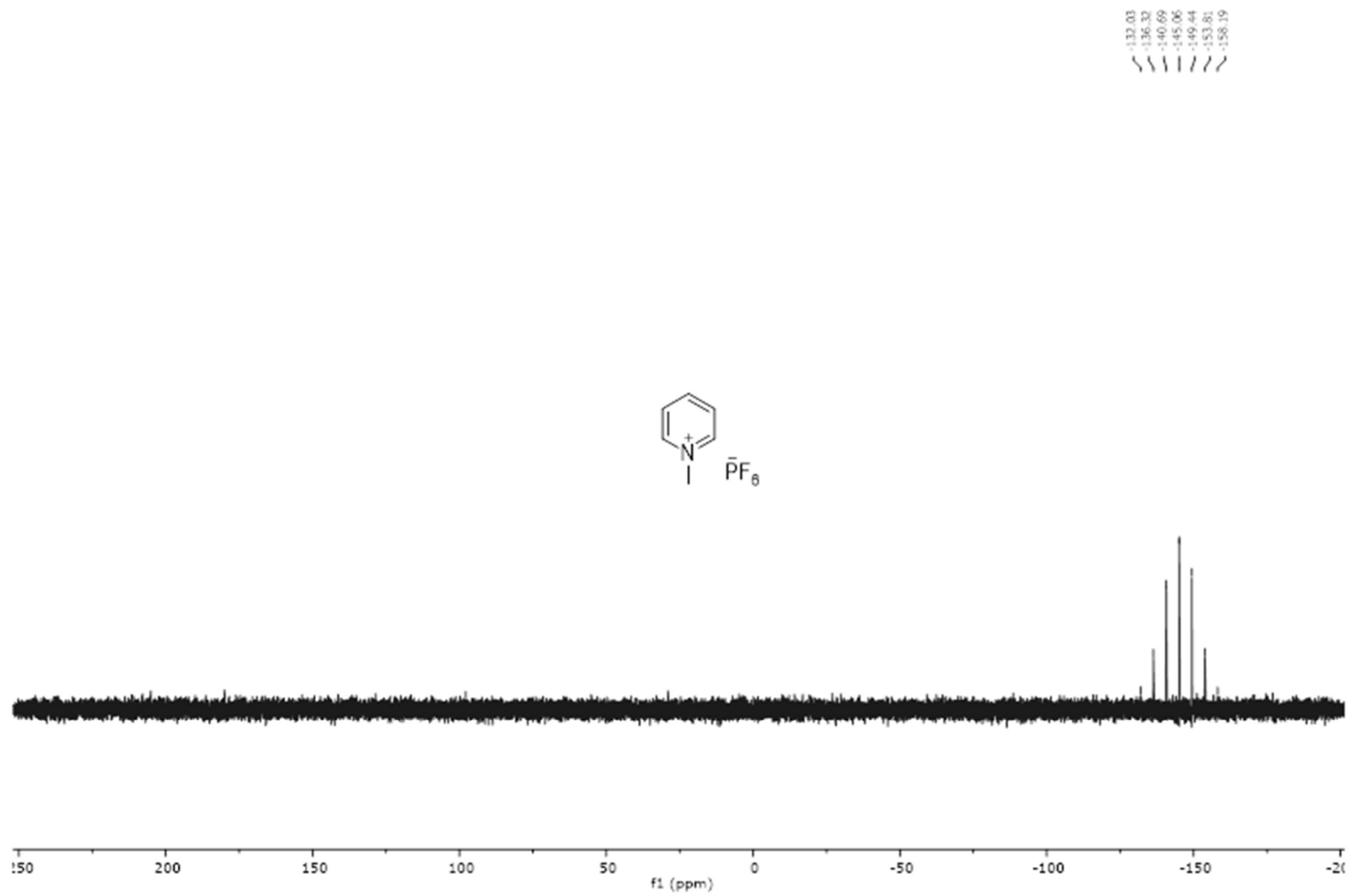
^1H NMR (D_2O , 400 MHz) spectrum of *N*-methylpyridinium iodide.



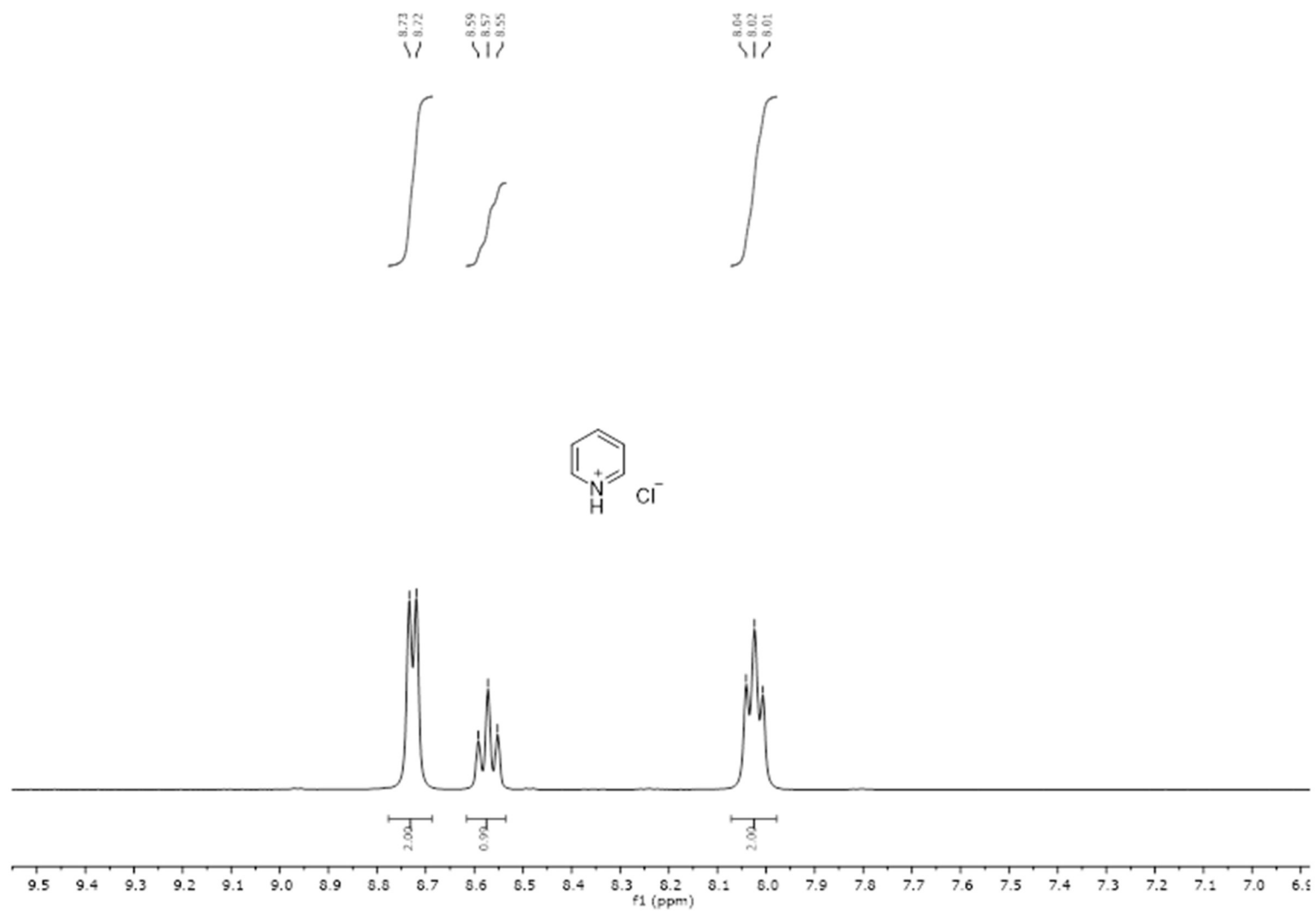
¹H NMR (D₂O, 400 MHz) spectrum of *N*-methylpyridinium hexafluorophosphate.



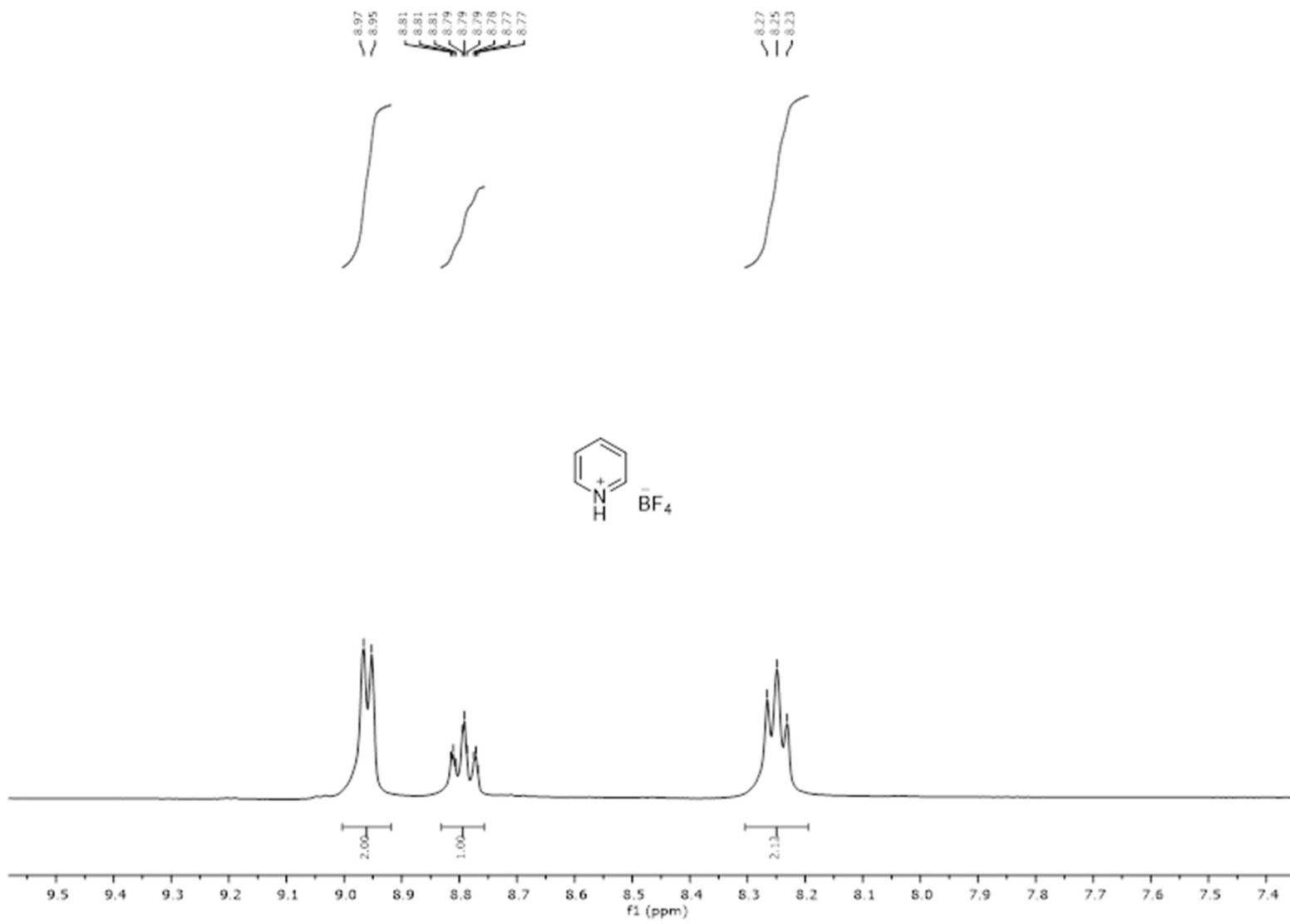
$^{19}\text{F}\{^1\text{H}\}$ NMR (D_2O , 376 MHz) spectrum of *N*-methylpyridinium hexafluorophosphate.



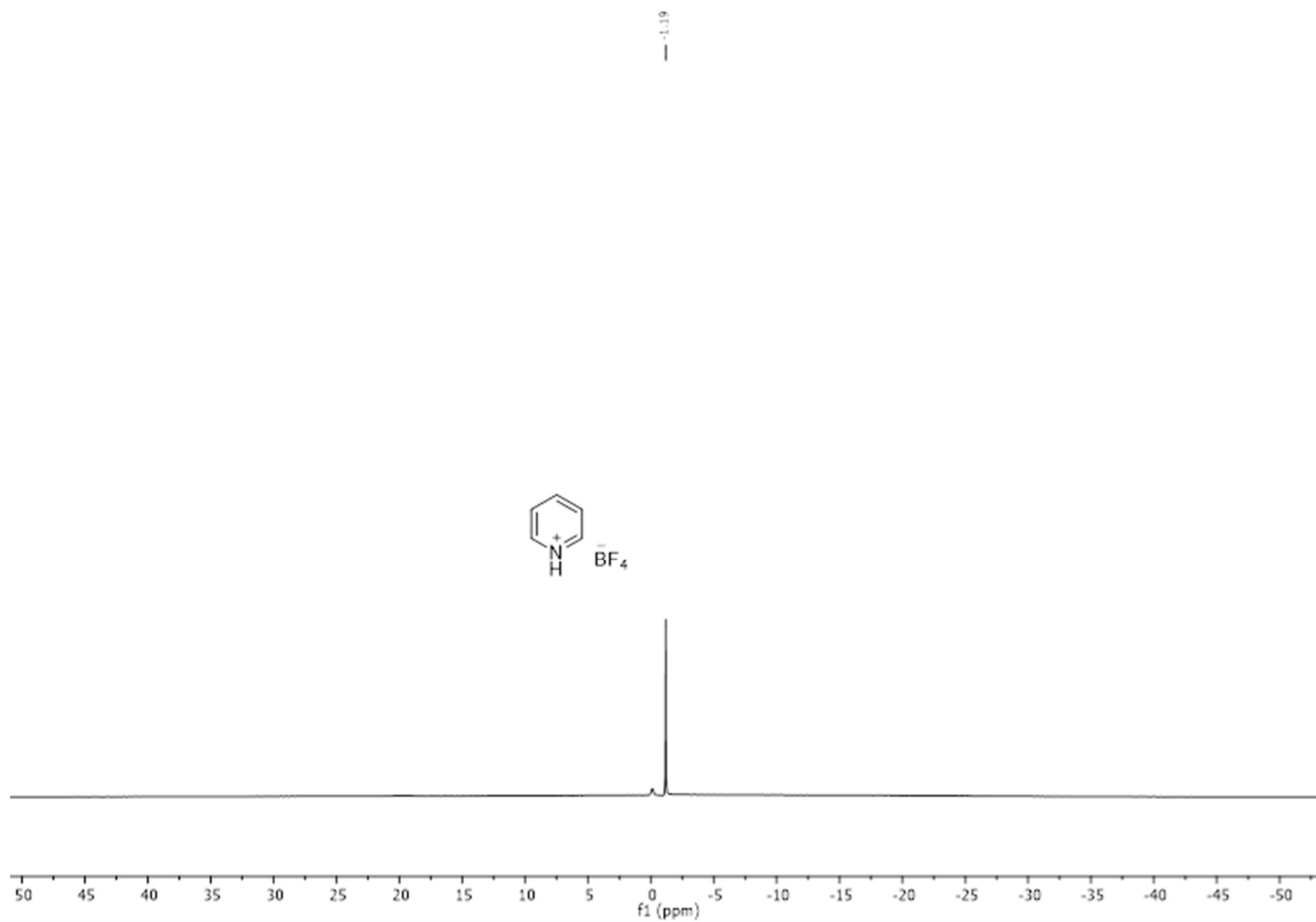
$^{31}\text{P}\{^1\text{H}\}$ NMR (D_2O , 162 MHz) spectrum of *N*-methylpyridinium hexafluorophosphate.



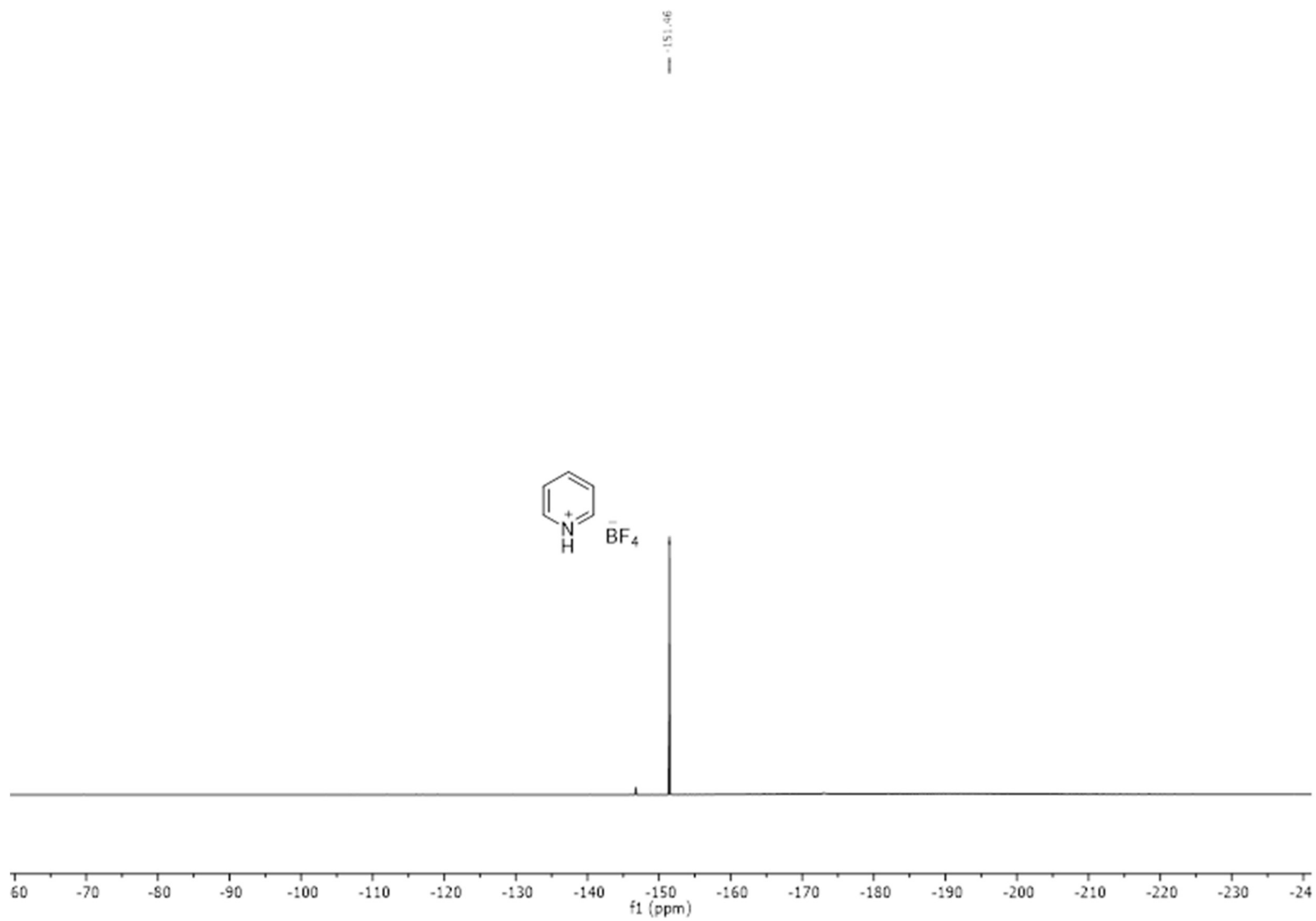
^1H NMR (D_2O , 400 MHz) spectrum of pyridinium chloride.



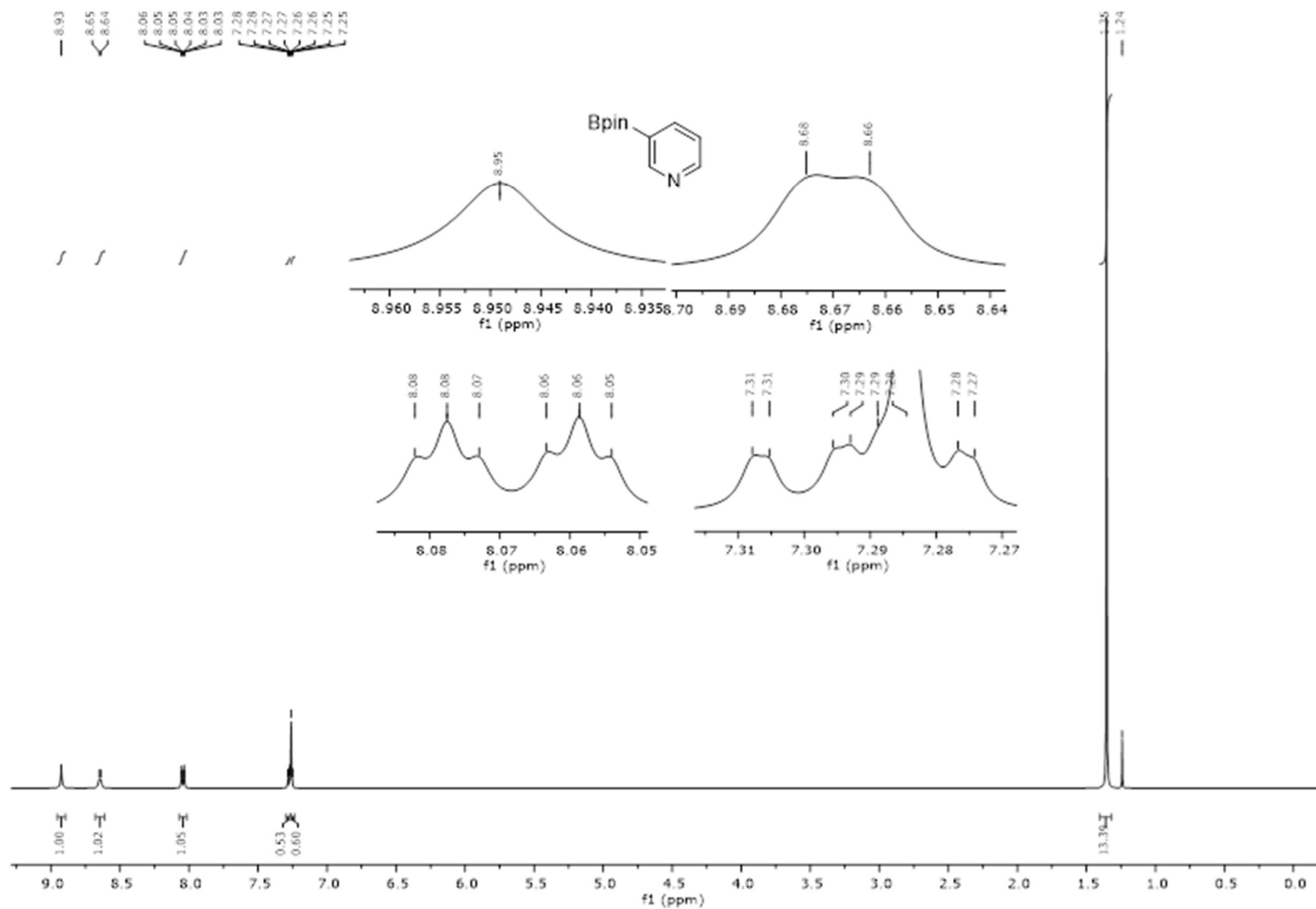
^1H NMR (D_2O , 400 MHz) spectrum of pyridinium tetrafluoroborate.



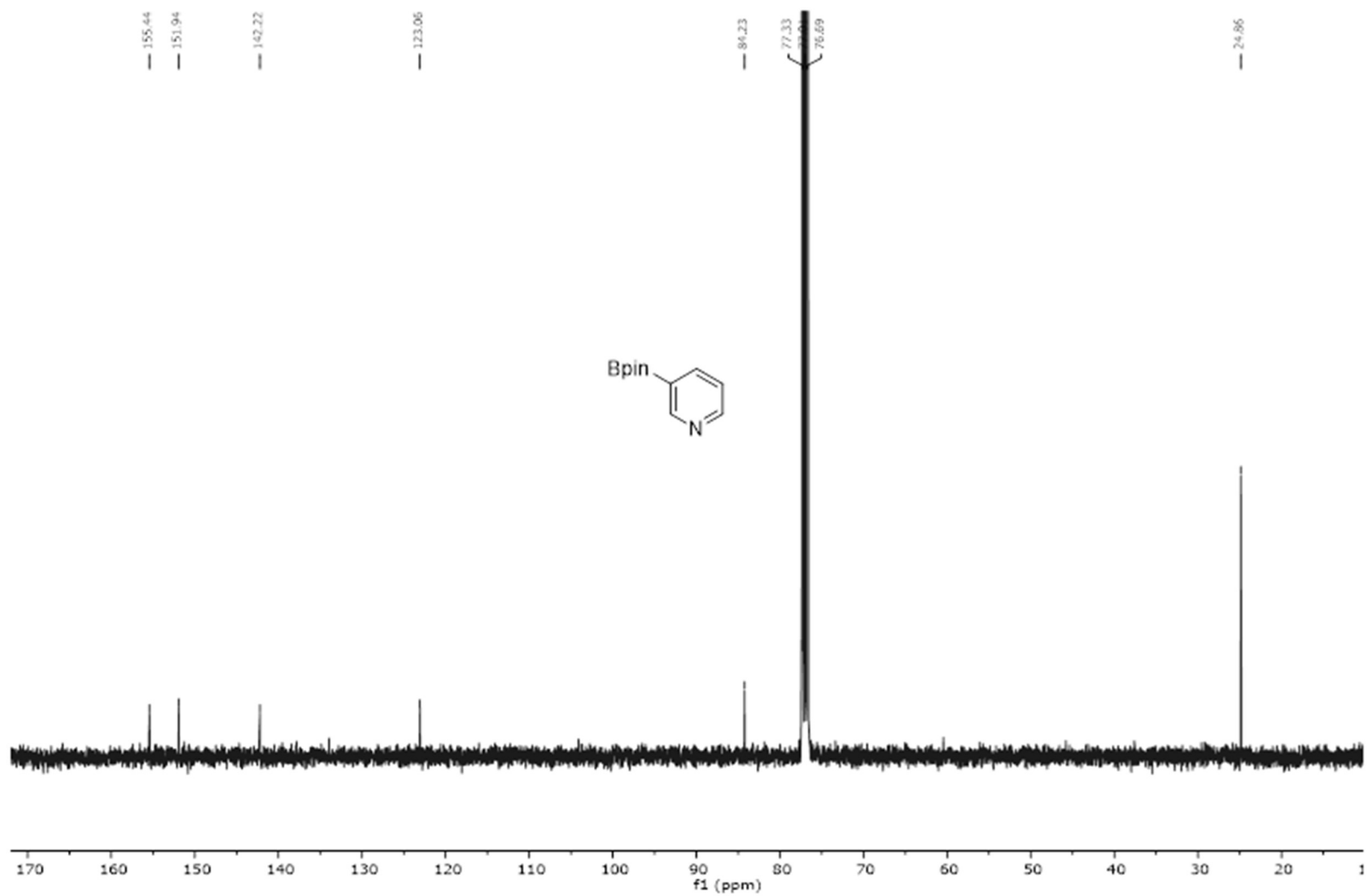
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of pyridinium tetrafluoroborate.



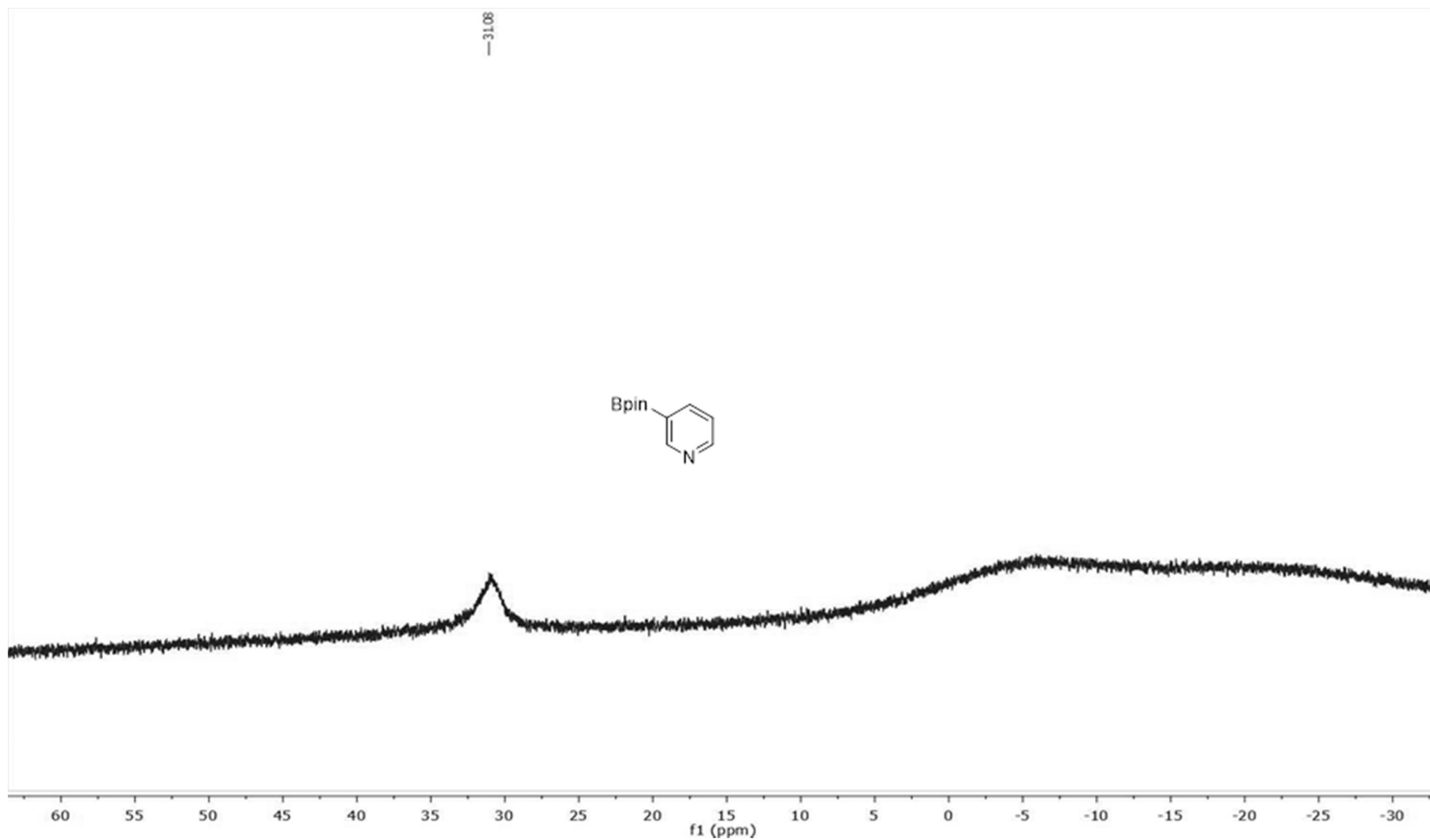
$^{19}\text{F}\{^1\text{H}\}$ NMR (D_2O , 376 MHz) spectrum of pyridinium tetrafluoroborate.



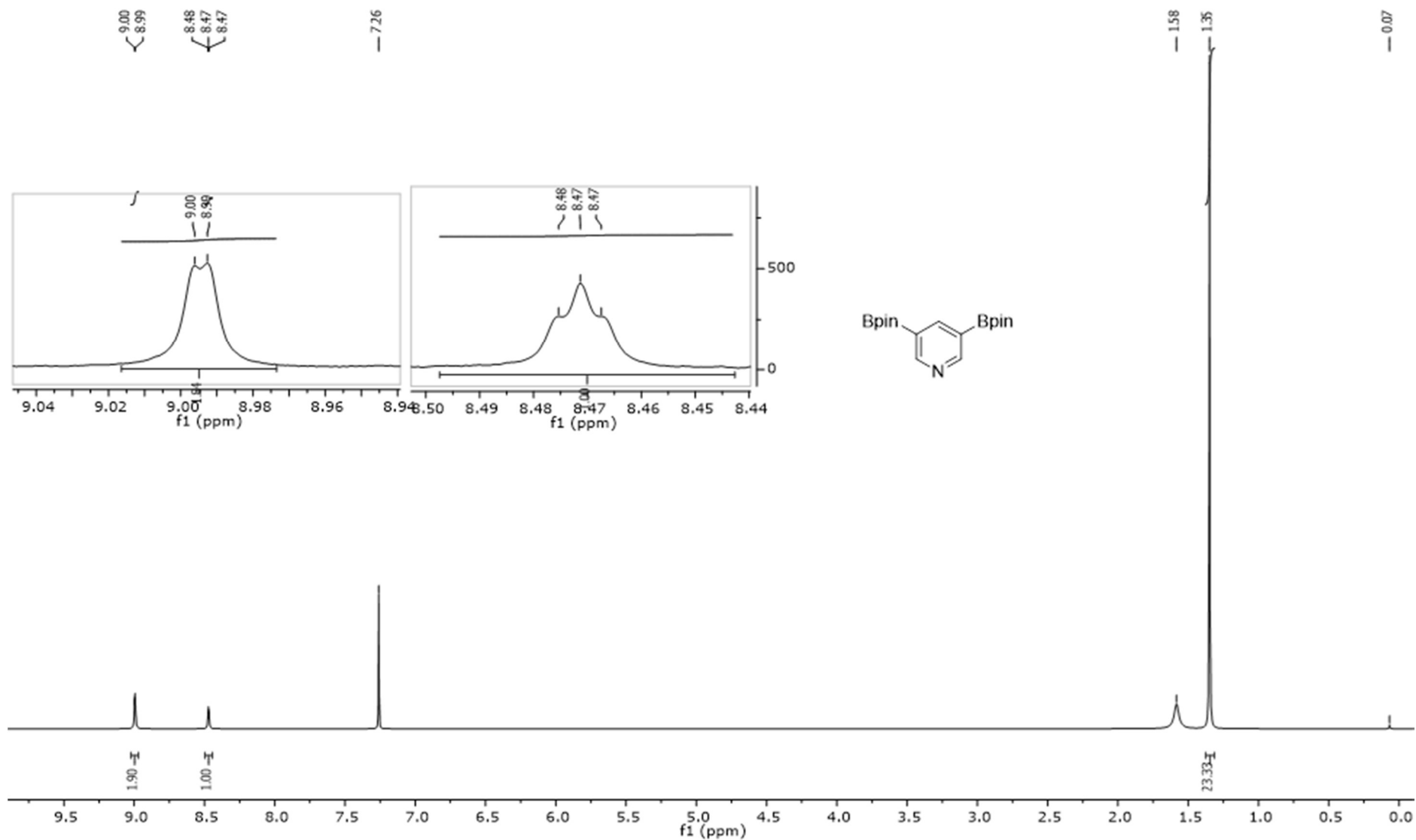
^1H NMR (CDCl_3 , 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (**1**).



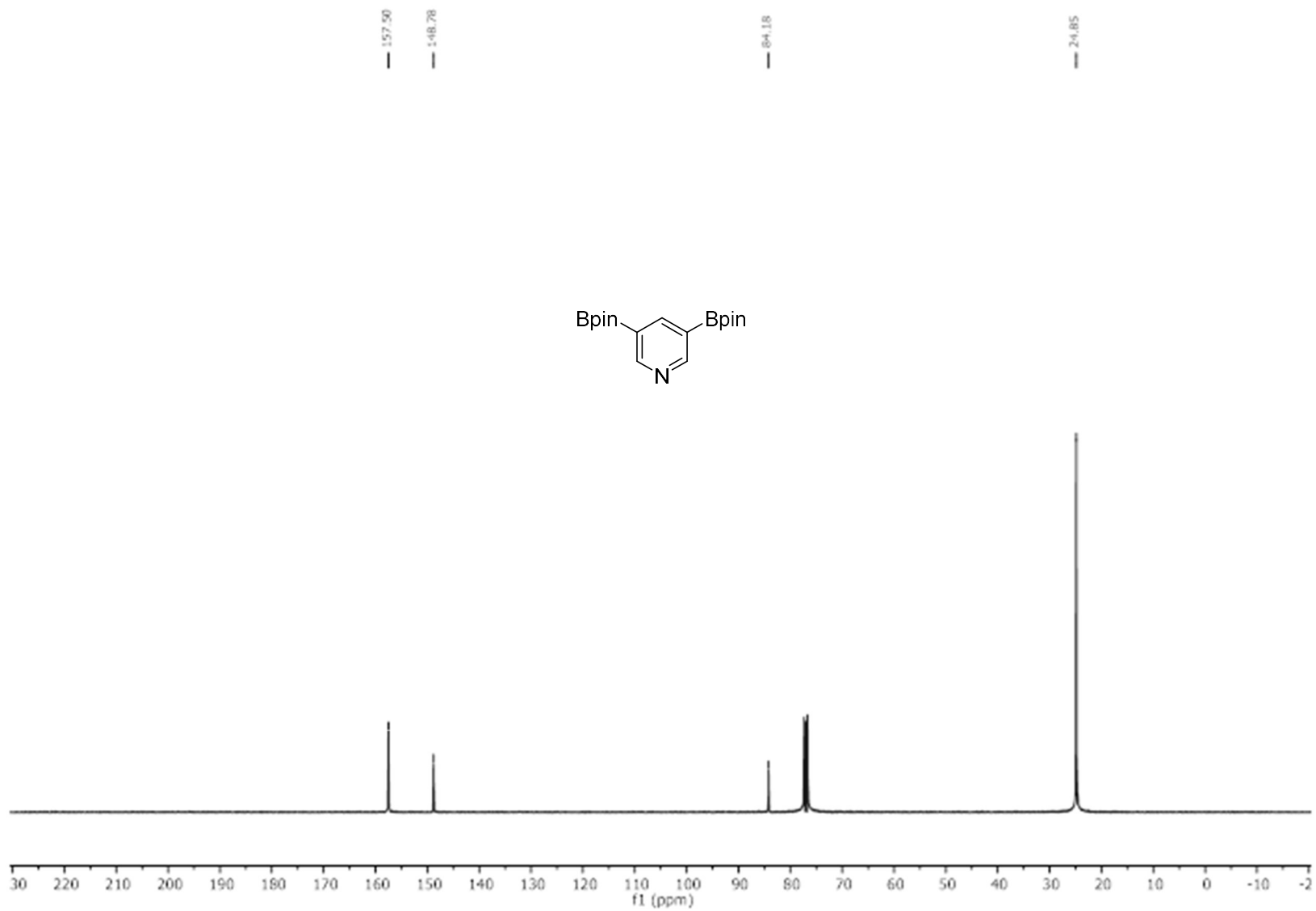
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**1**).



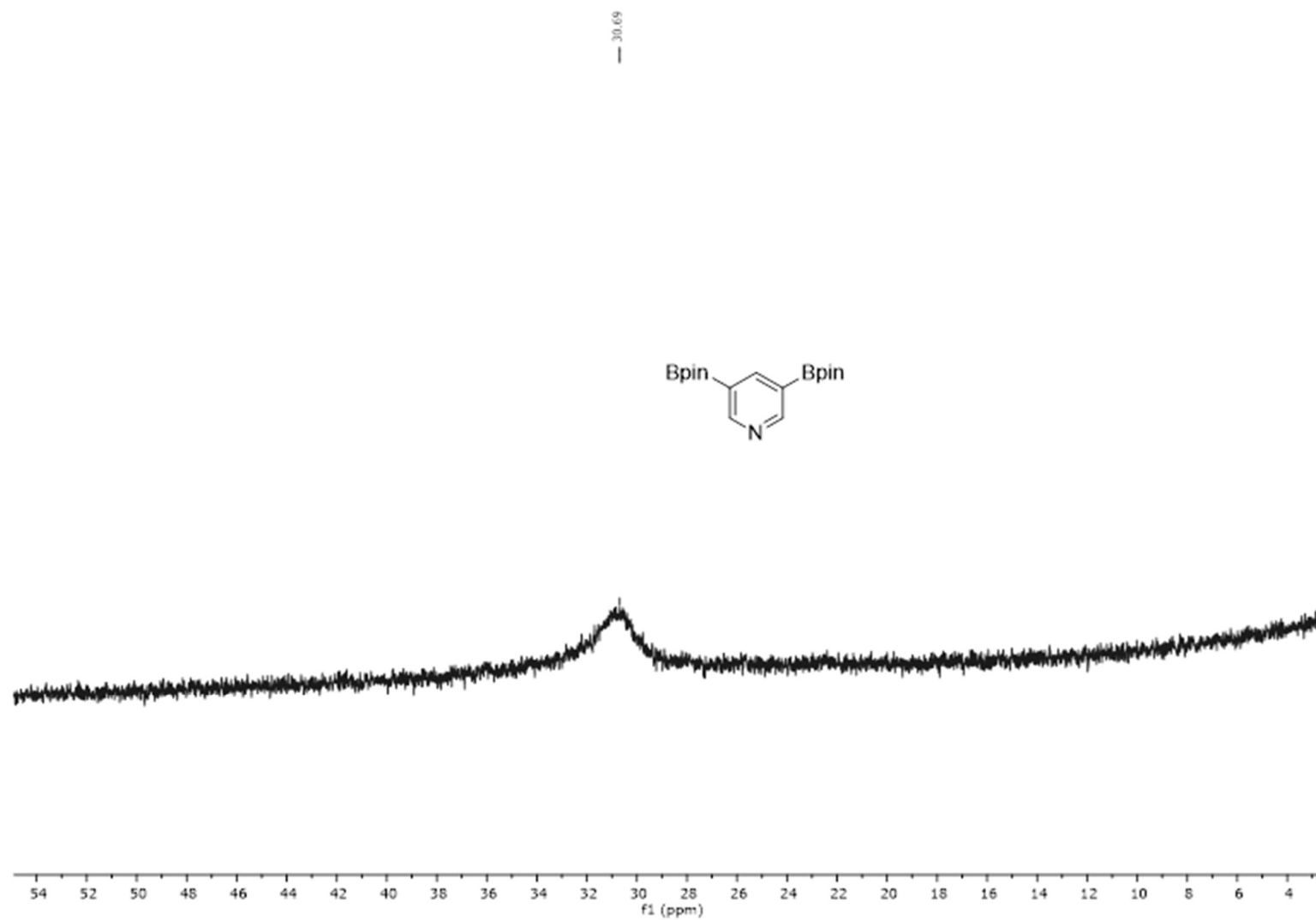
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (**1**).



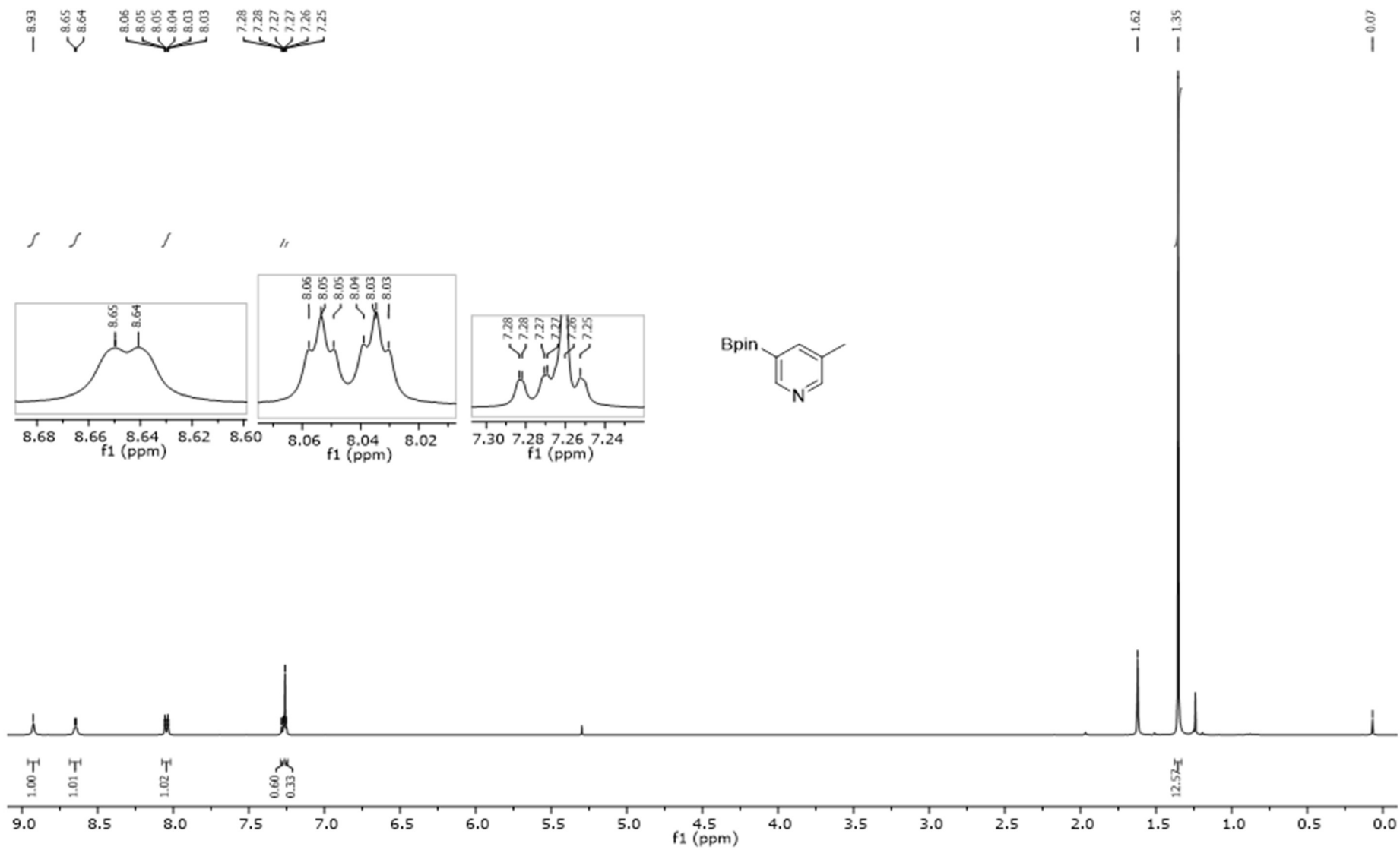
^1H NMR (CDCl_3 , 400 MHz) spectrum of 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**2**).



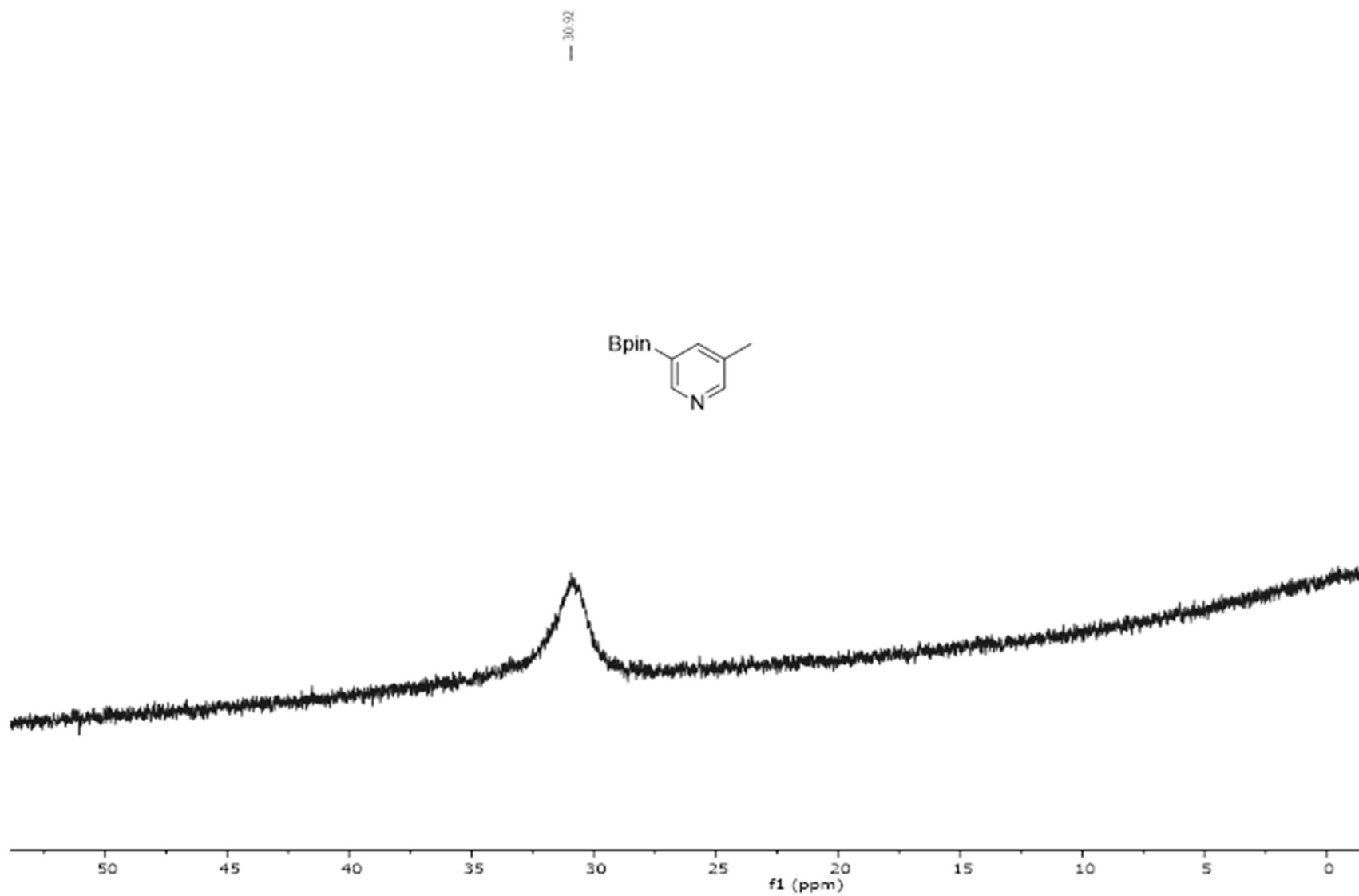
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**2**).



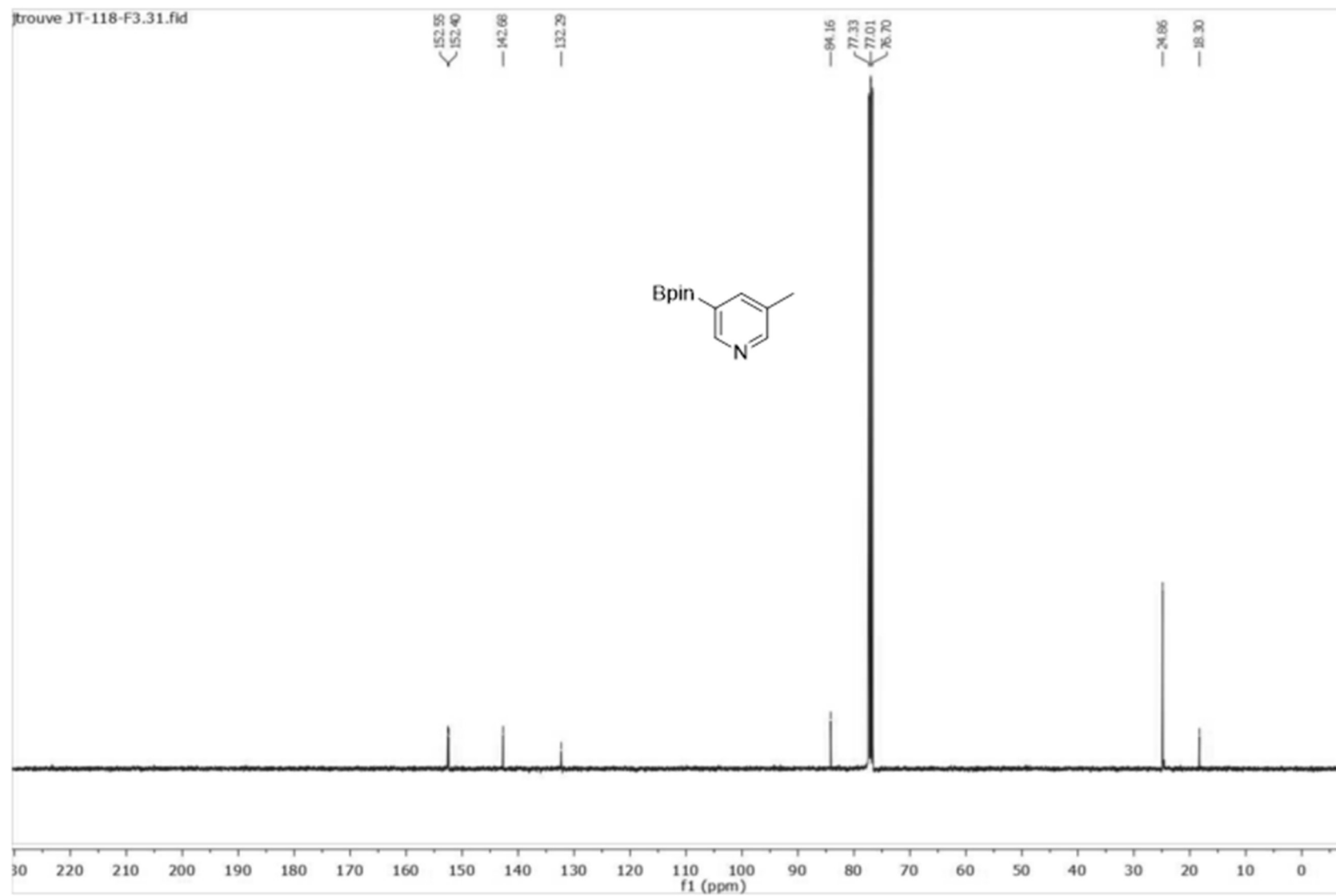
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (**2**).



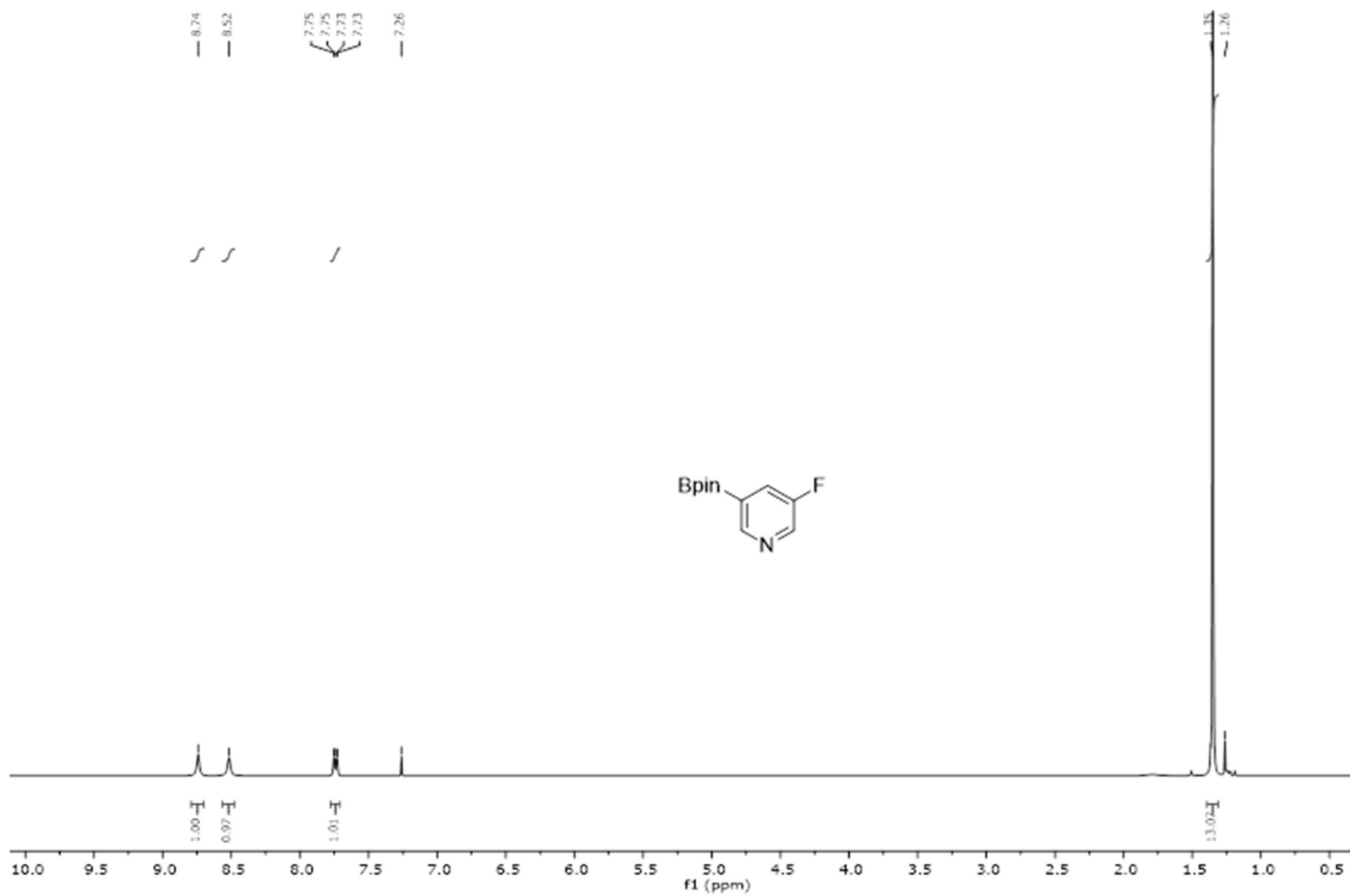
^1H NMR (CDCl_3 , 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylpyridine (**5a**).



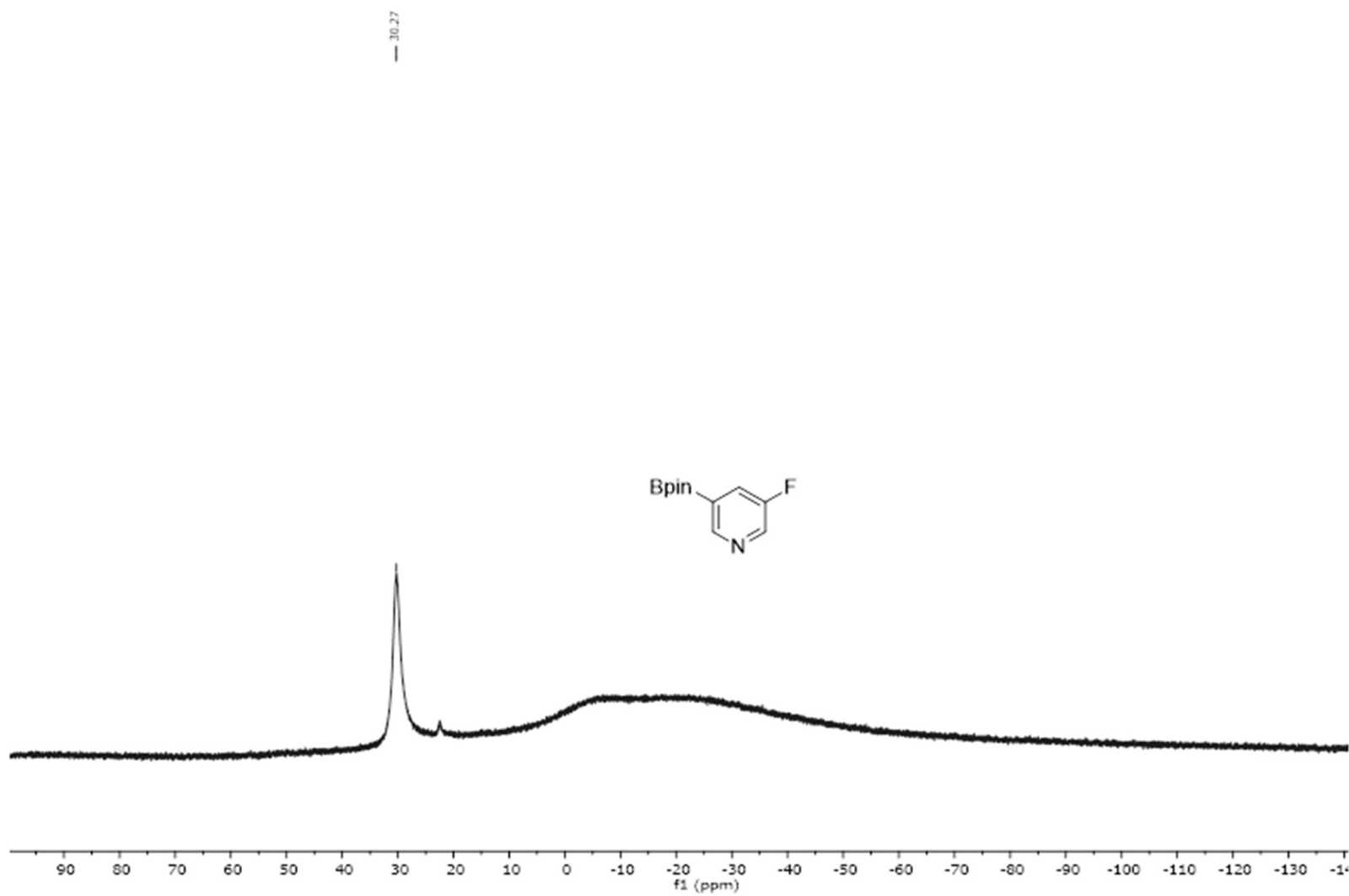
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylpyridine (**5a**).



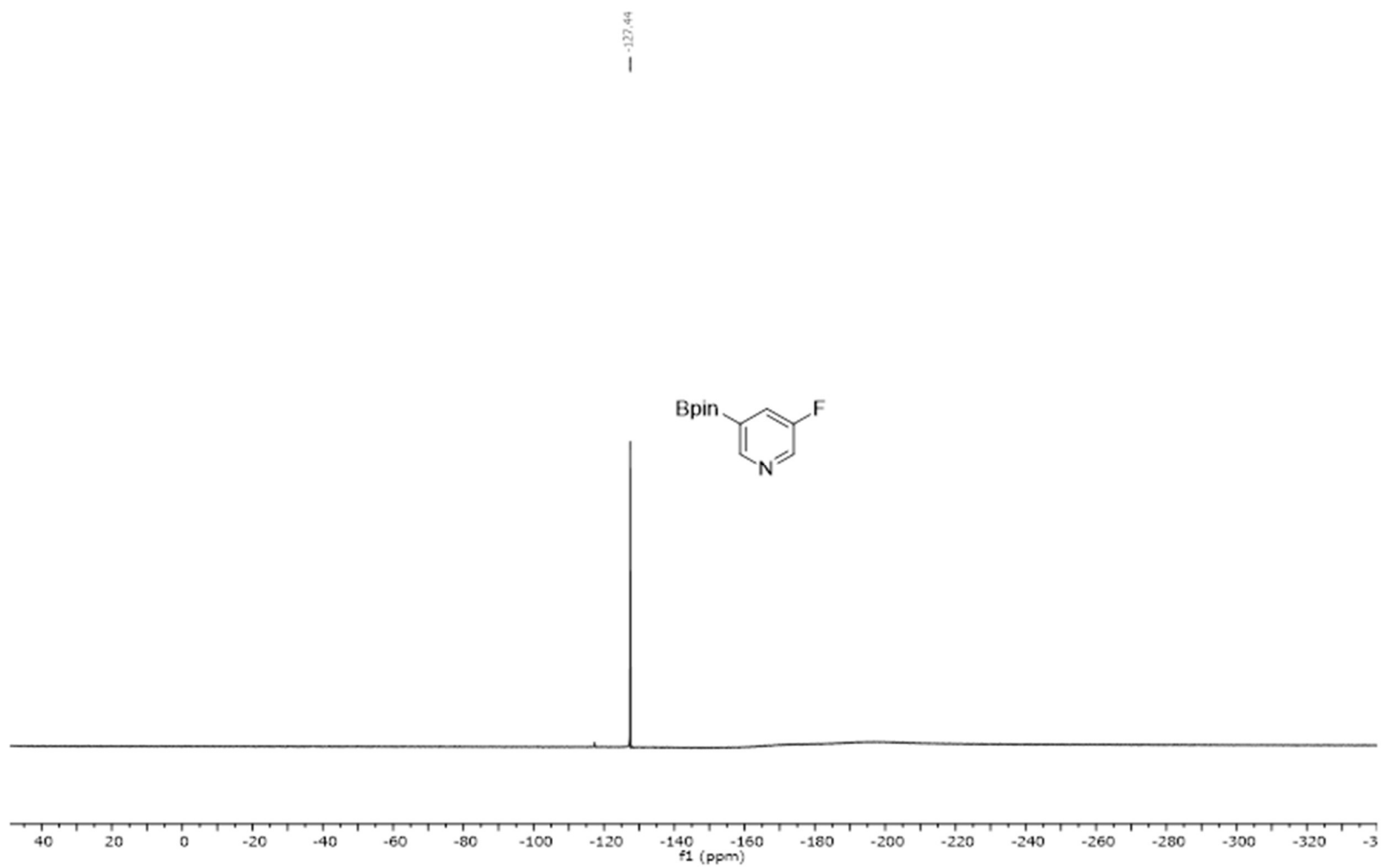
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylpyridine (**5a**).



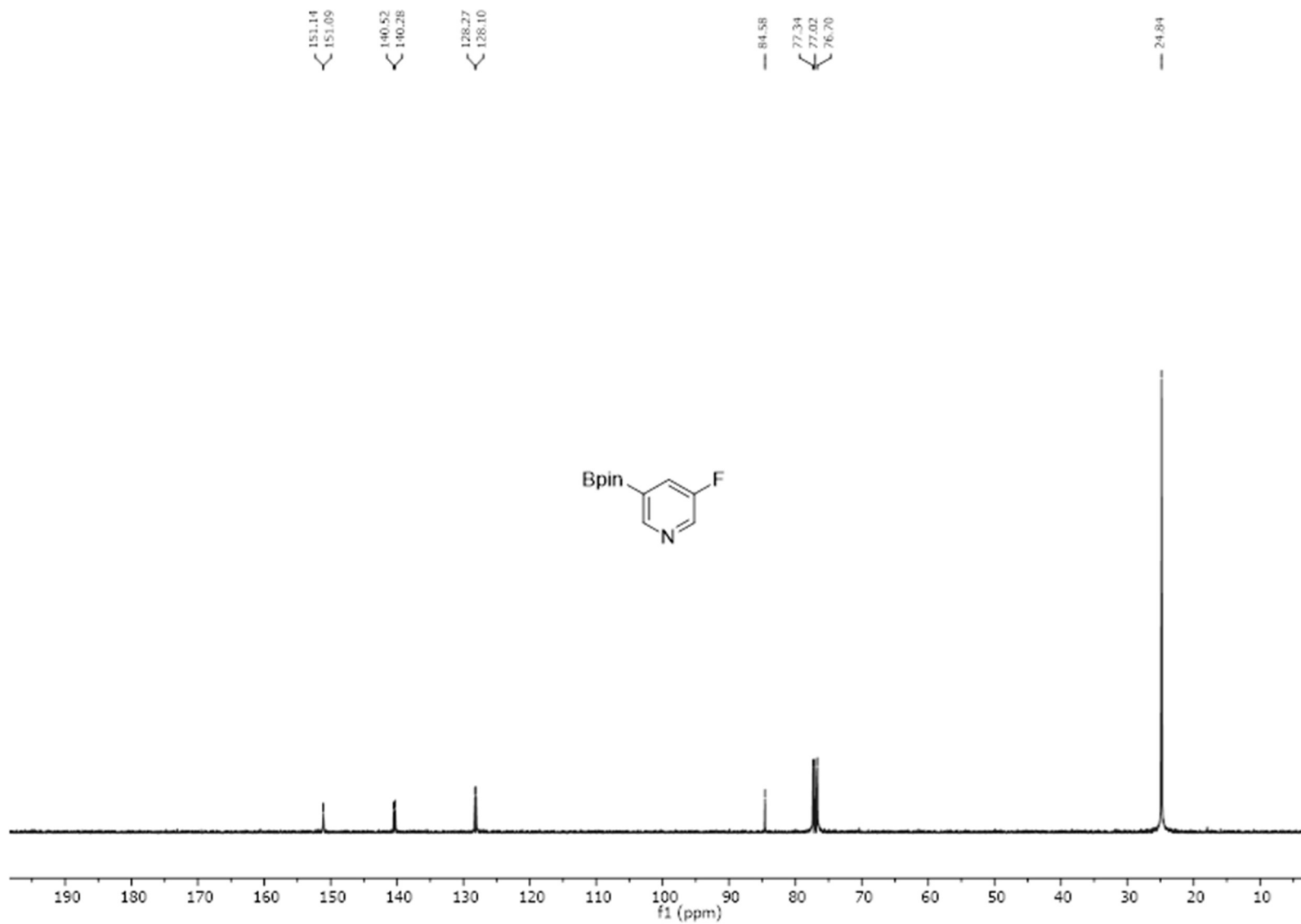
¹H NMR (CDCl₃, 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-fluoropyridine (**5b**).



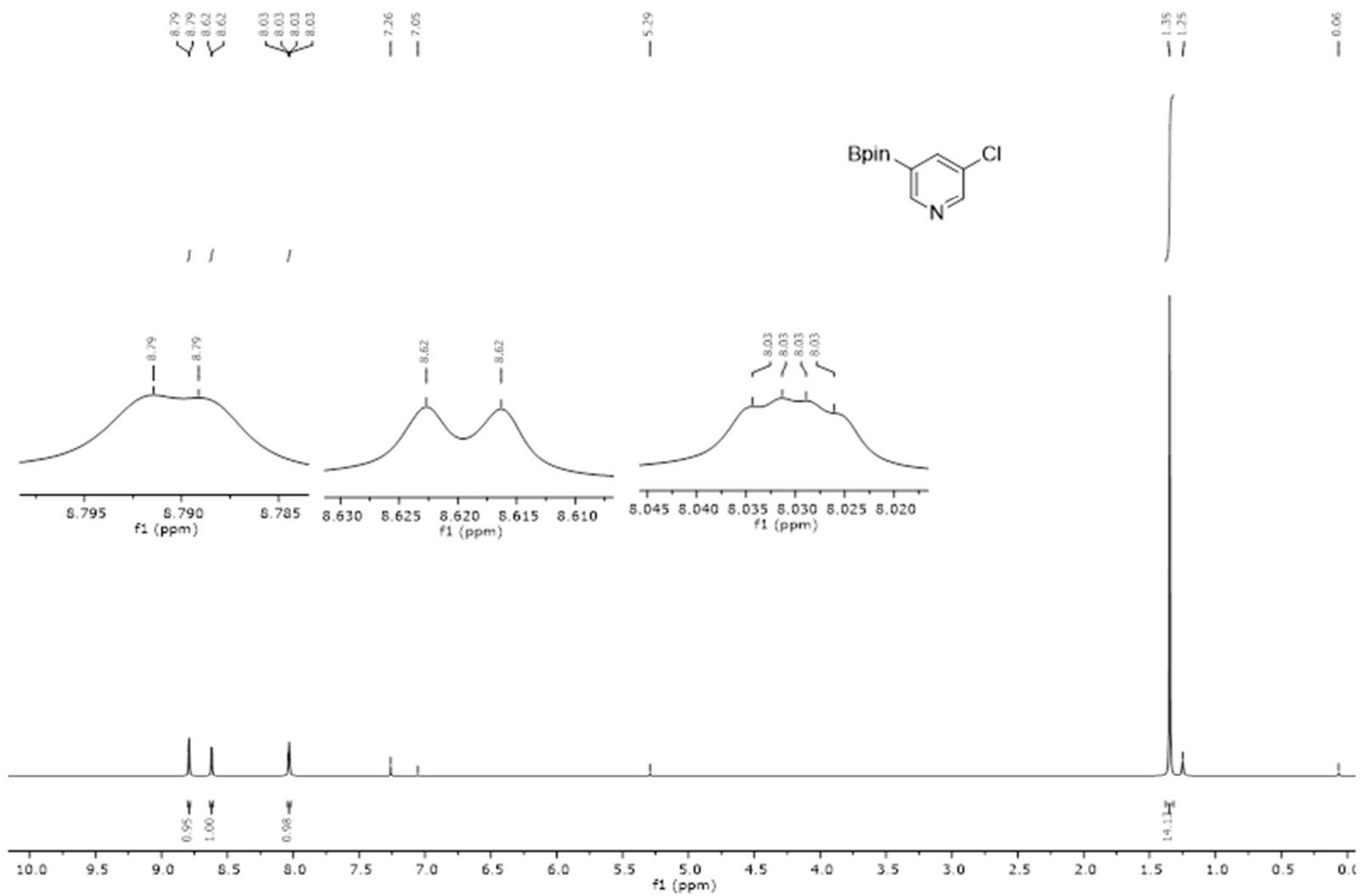
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-fluoropyridine (**5b**).



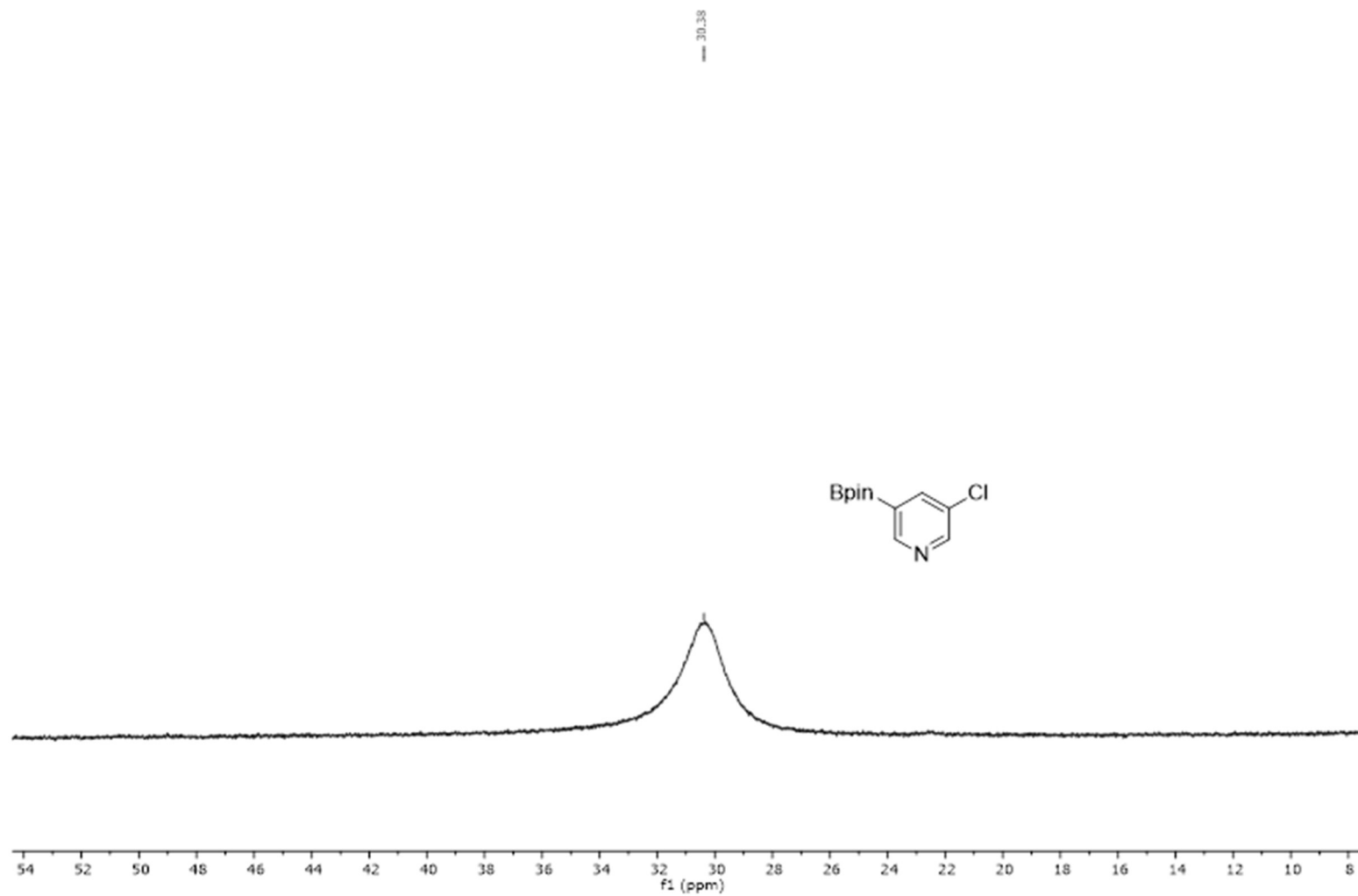
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-fluoropyridine (**5b**).



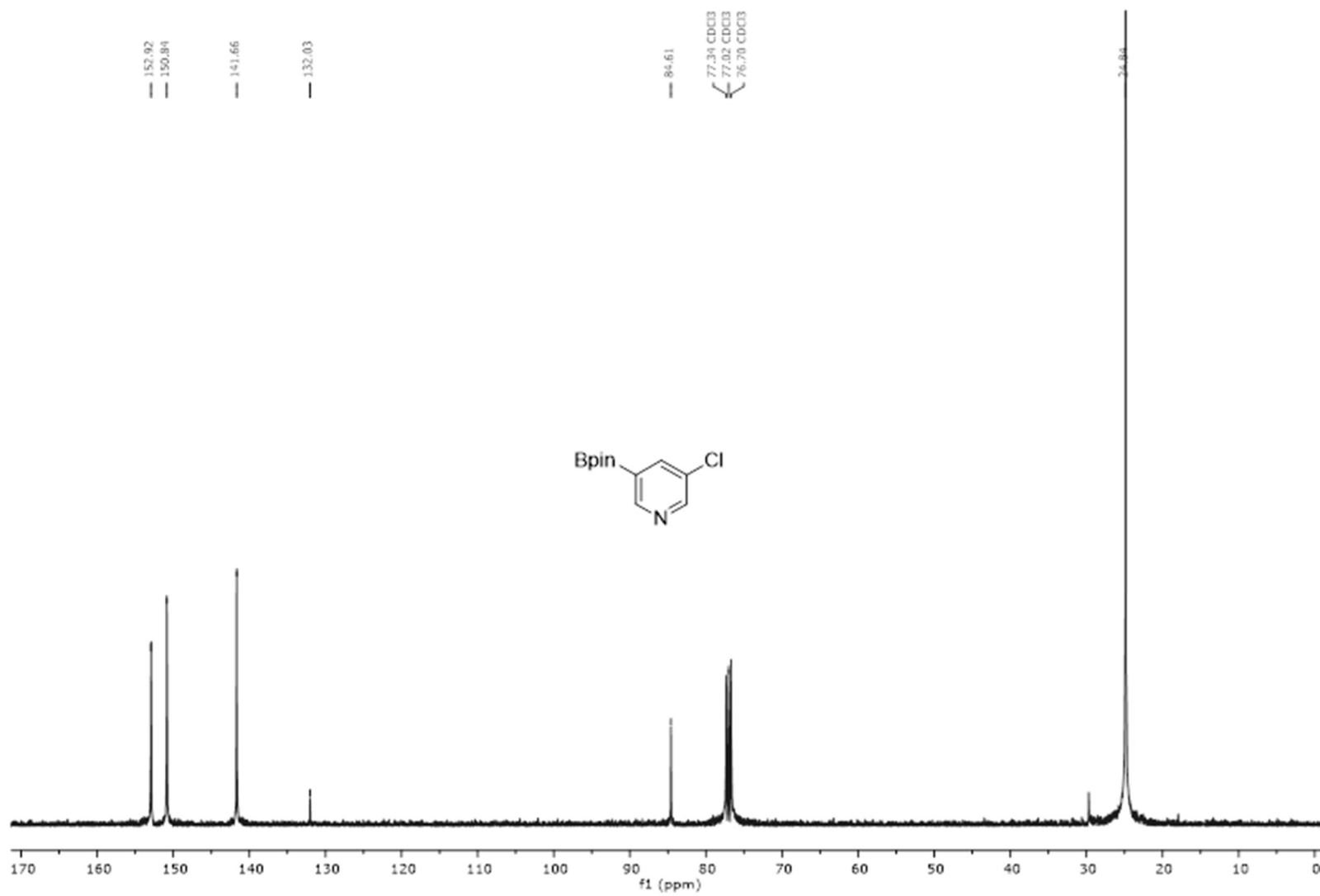
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-fluoropyridine (**5b**).



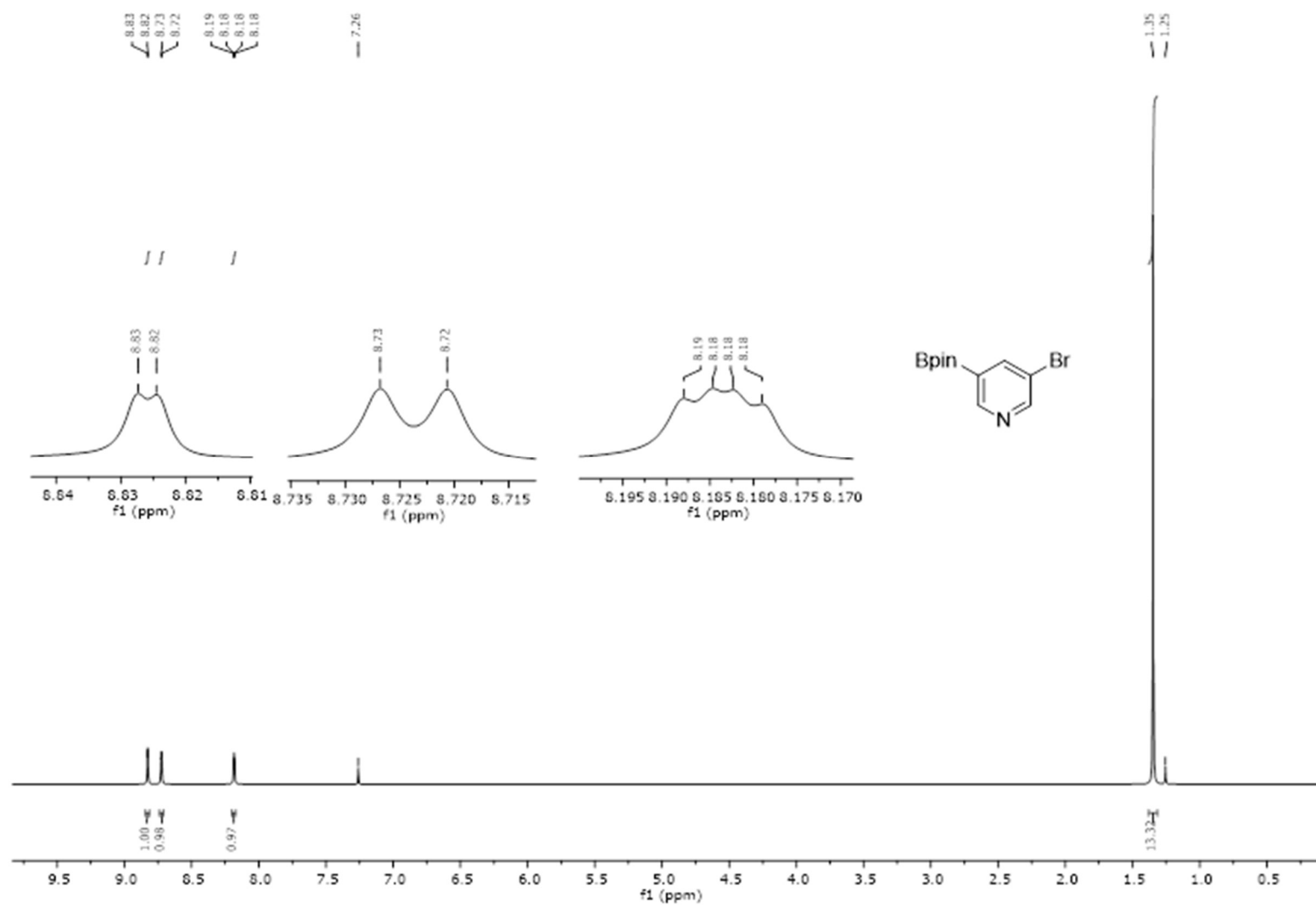
¹H NMR (CDCl₃, 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-chloropyridine (**5c**).



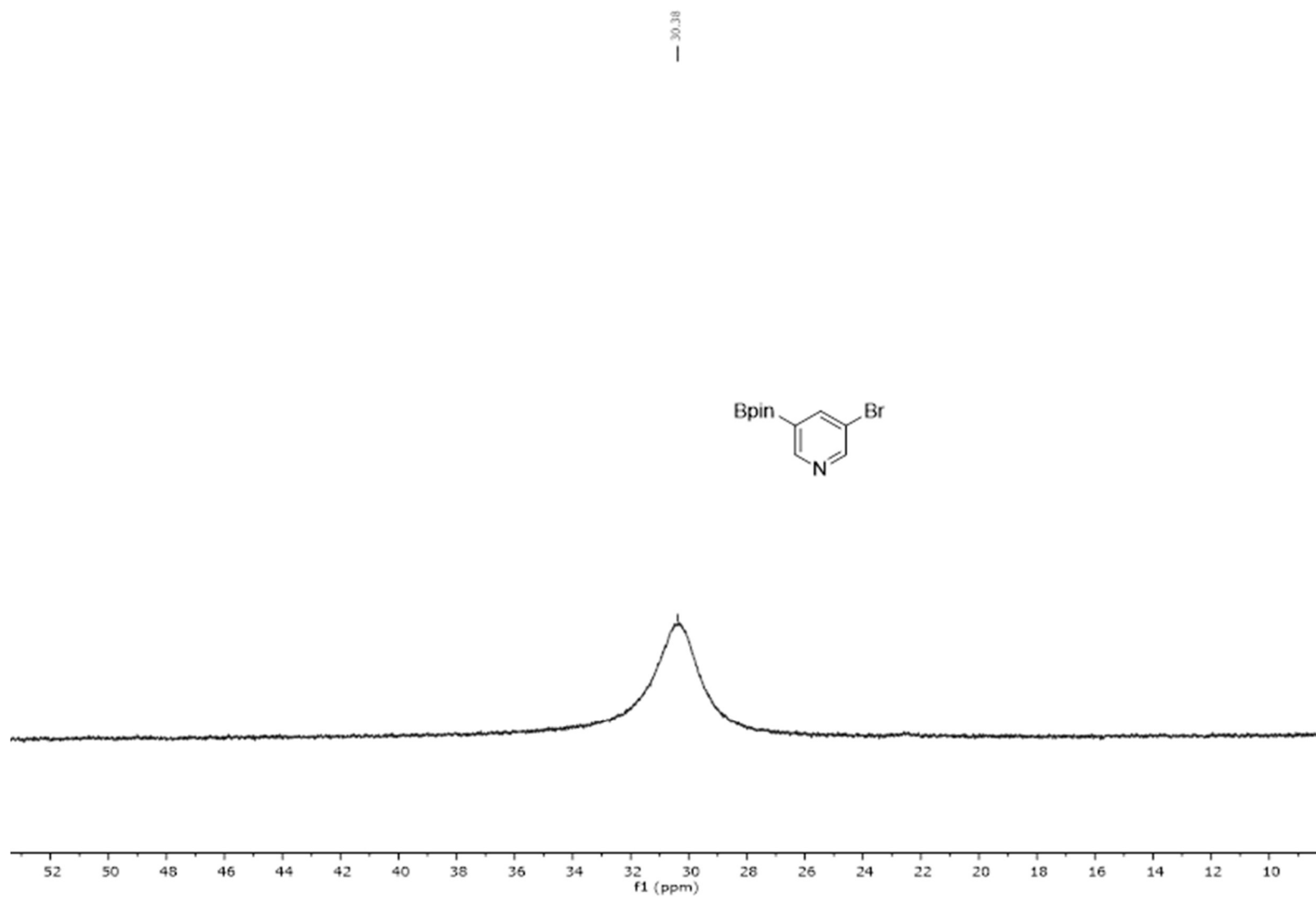
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-chloropyridine (**5c**).



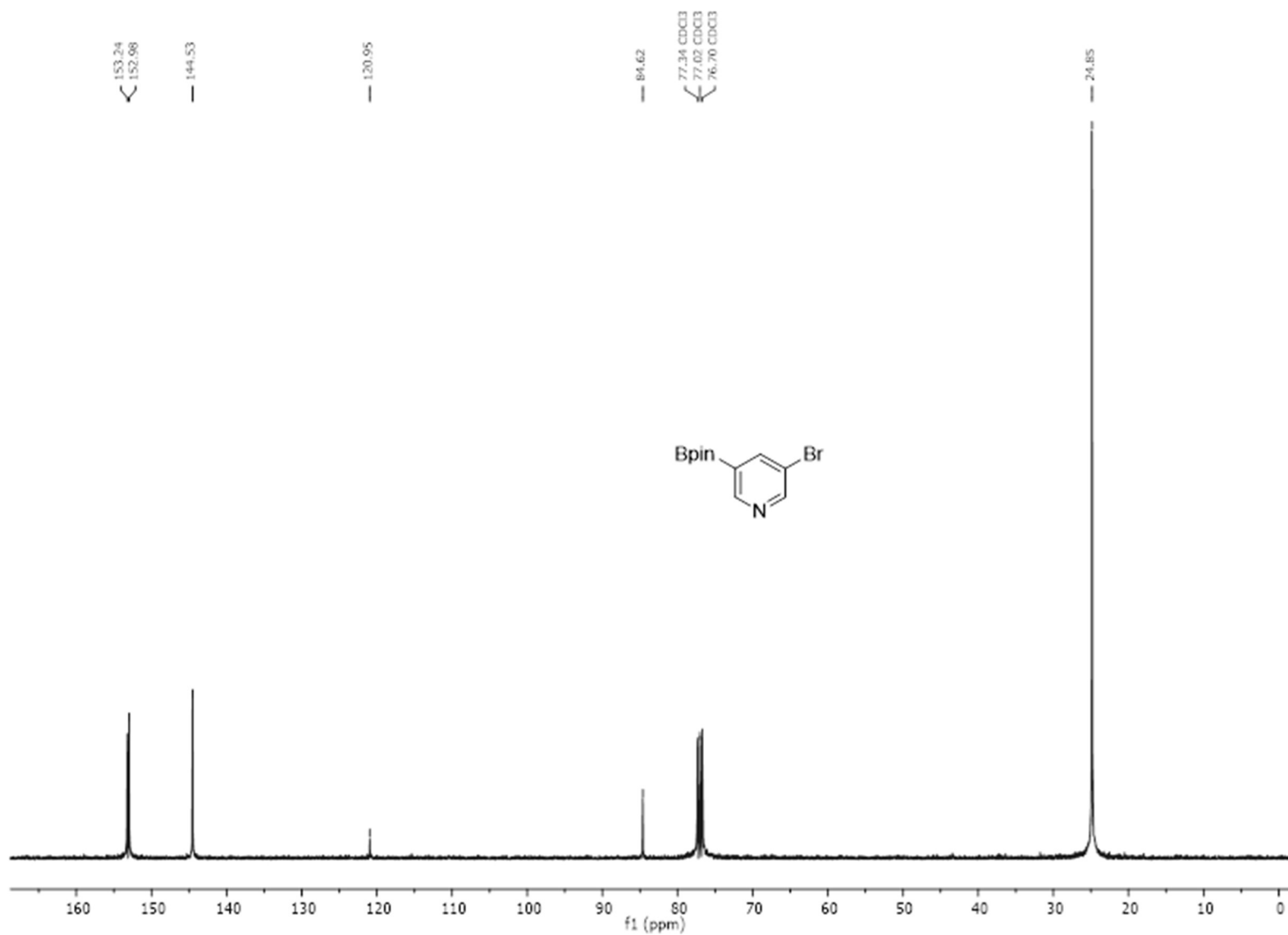
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-chloropyridine (**5c**).



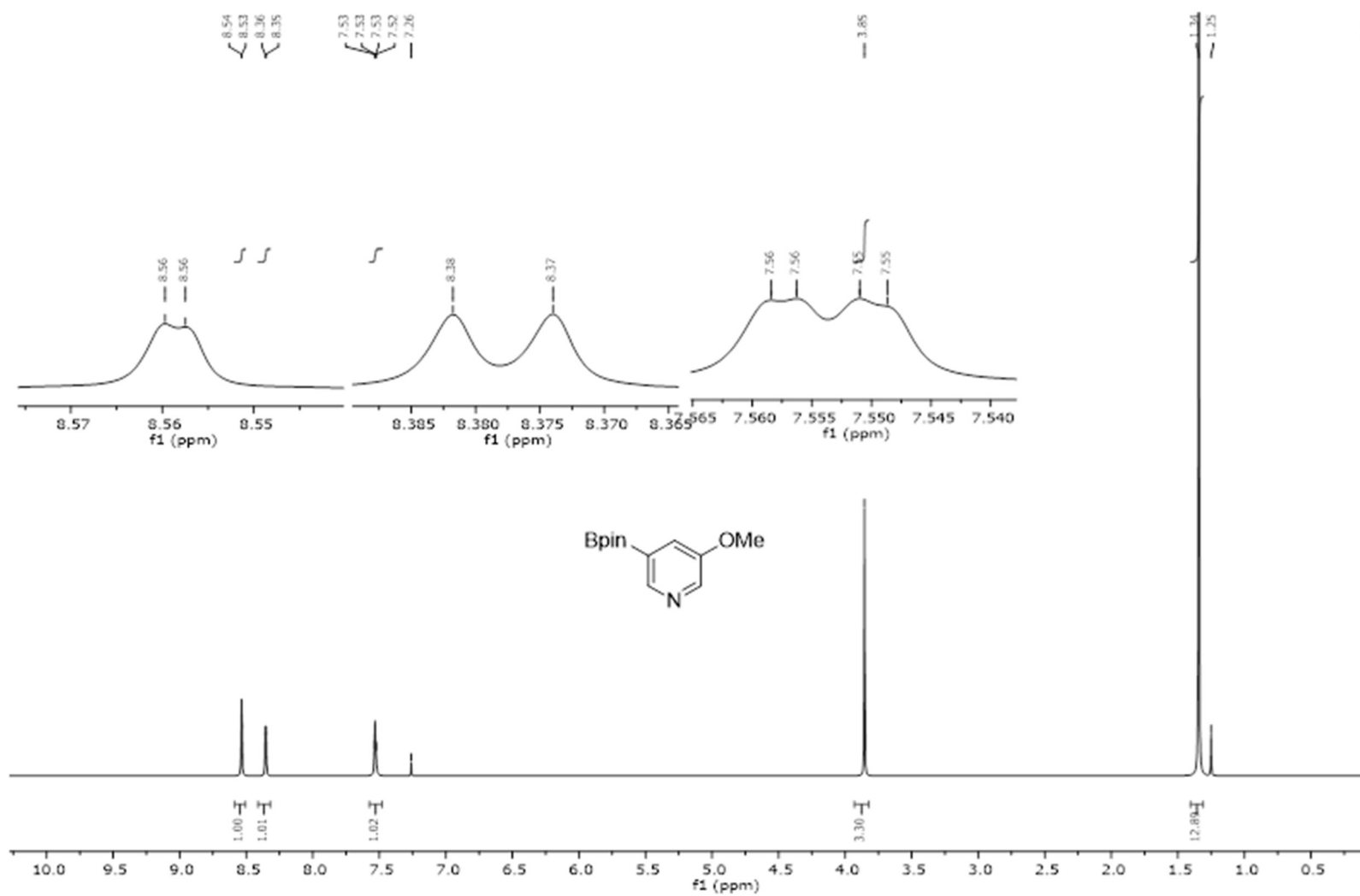
^1H NMR (CDCl_3 , 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-bromopyridine (**5d**).



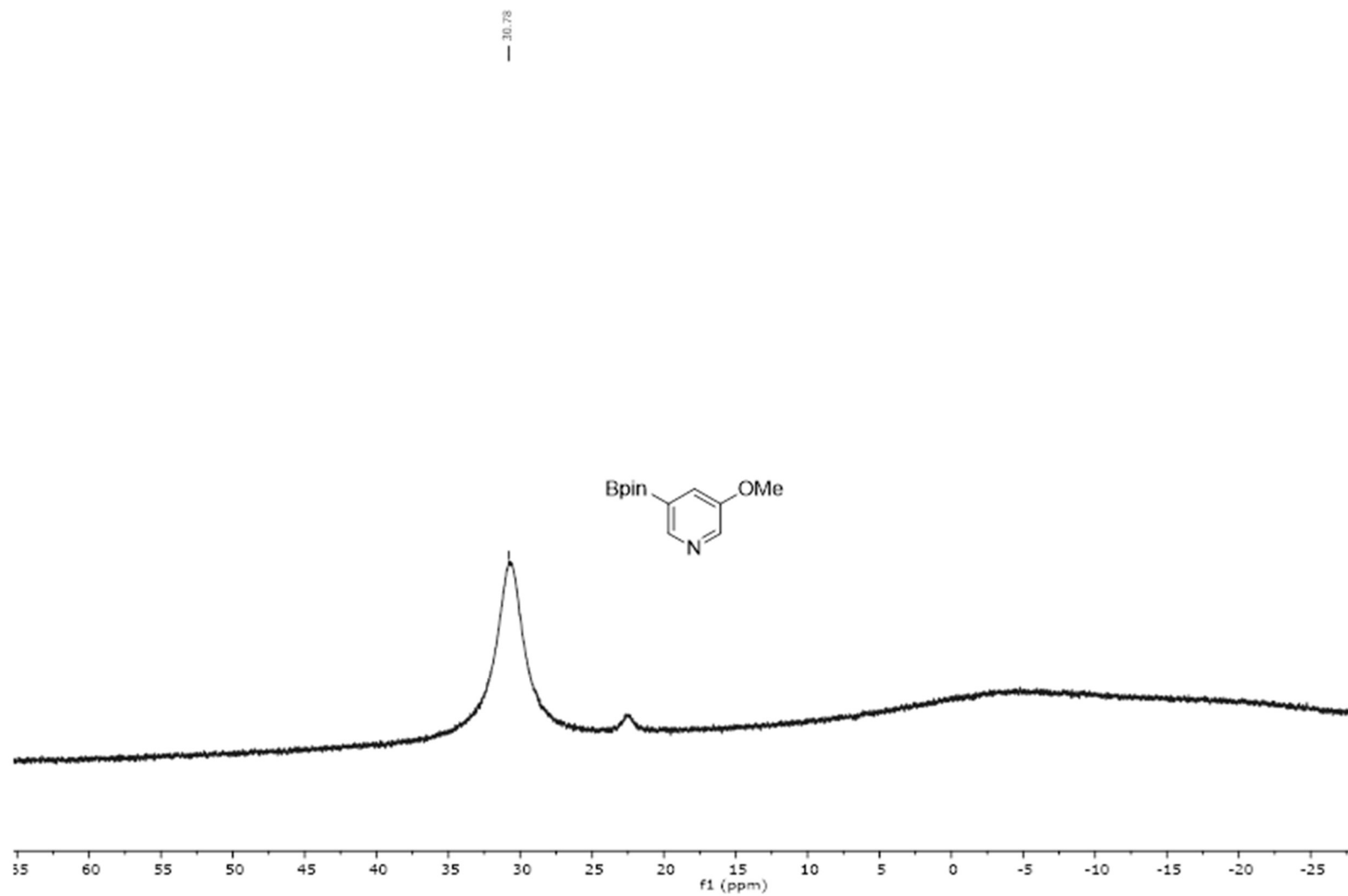
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-bromopyridine (**5d**).



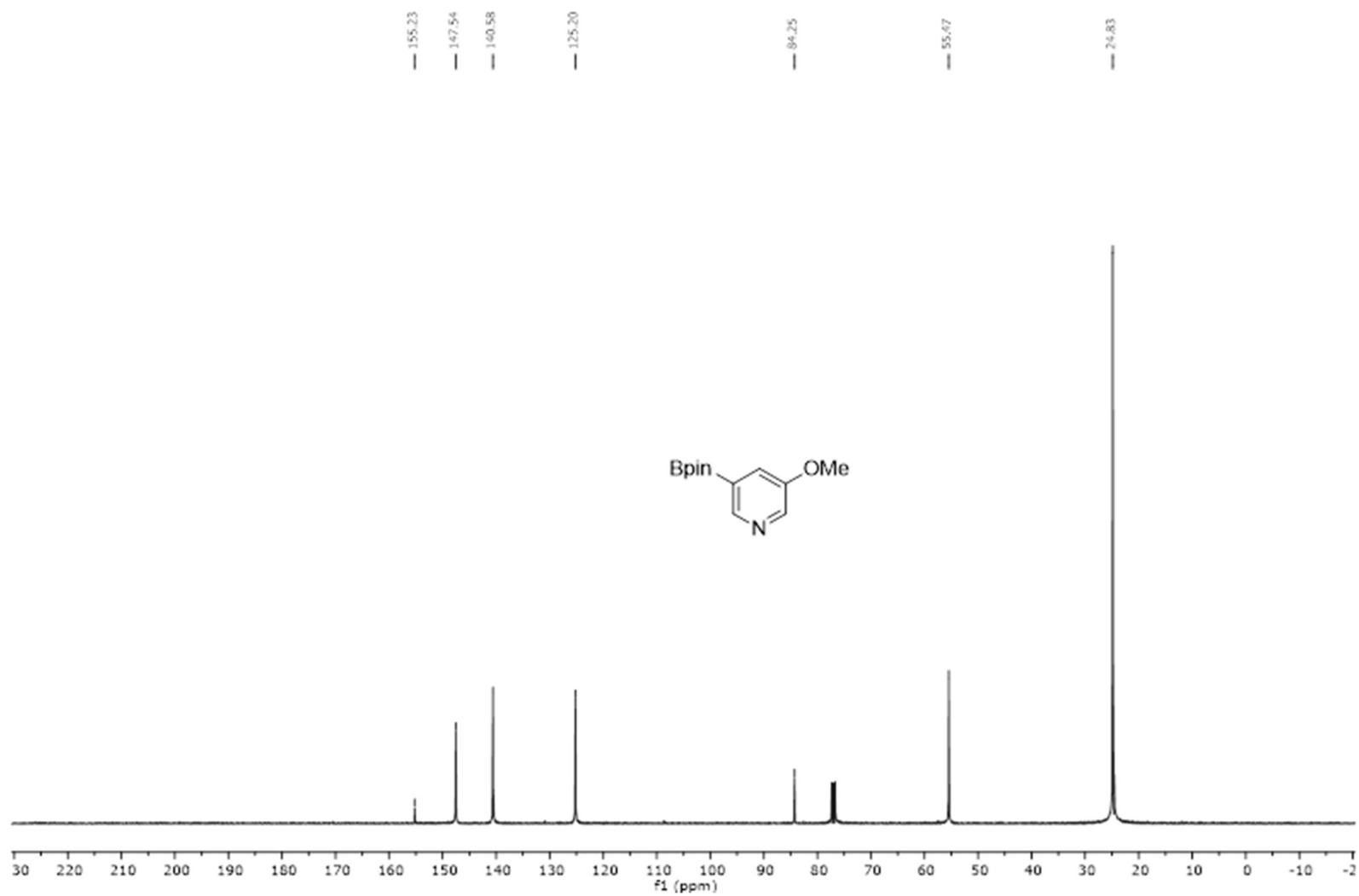
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-bromopyridine (**5d**).



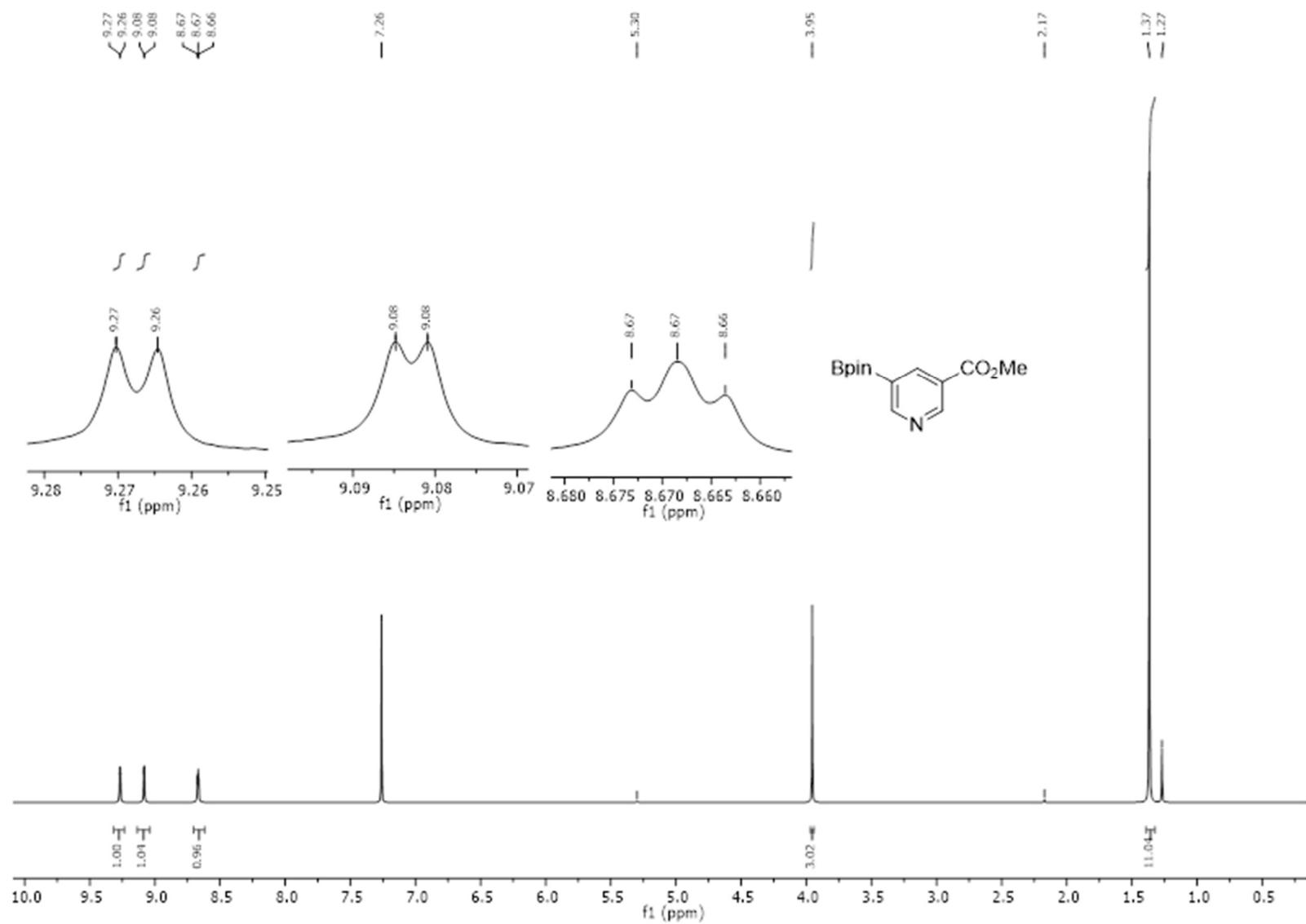
^1H NMR (CDCl_3 , 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methoxypyridine (**5e**).



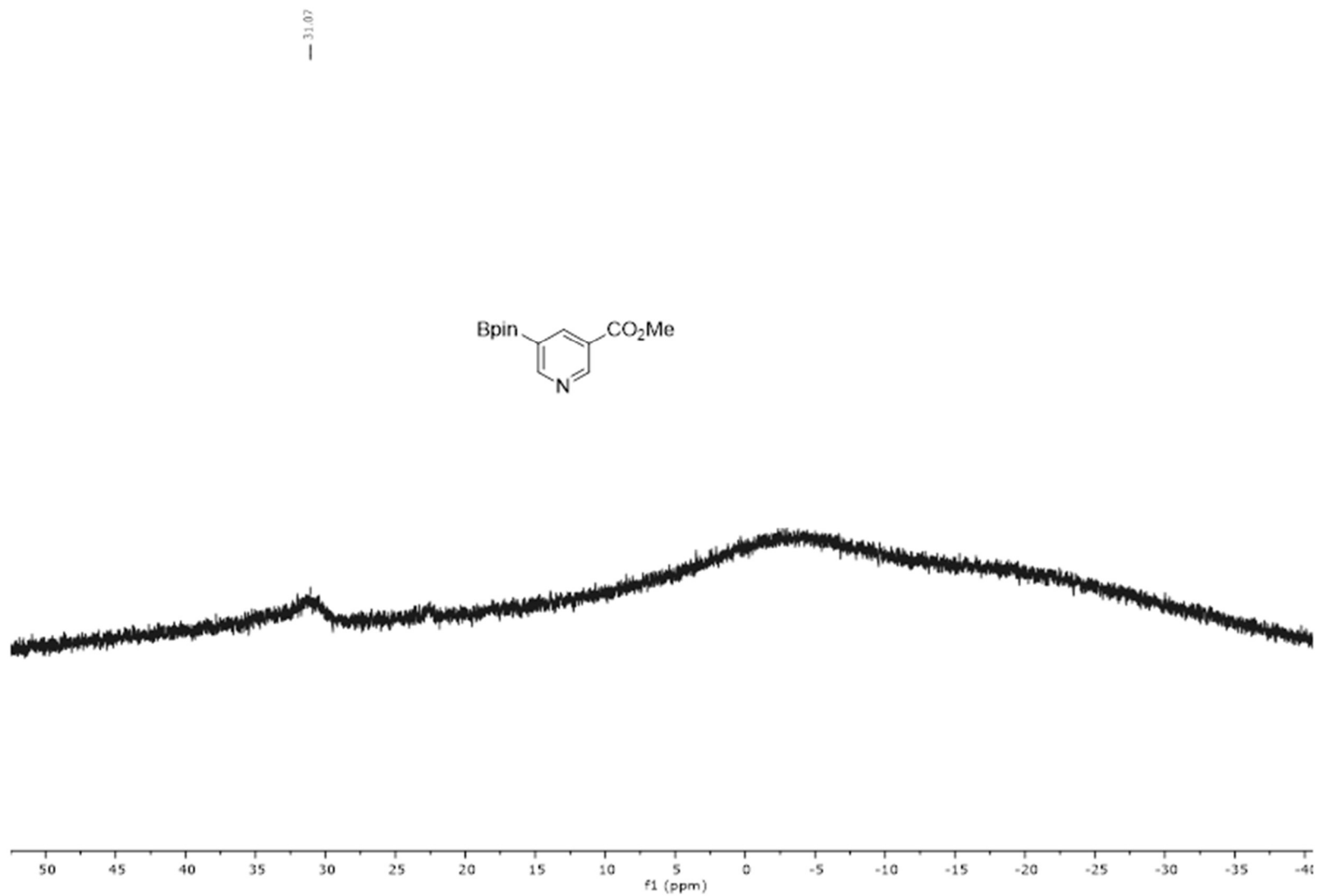
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methoxypyridine (**5e**).



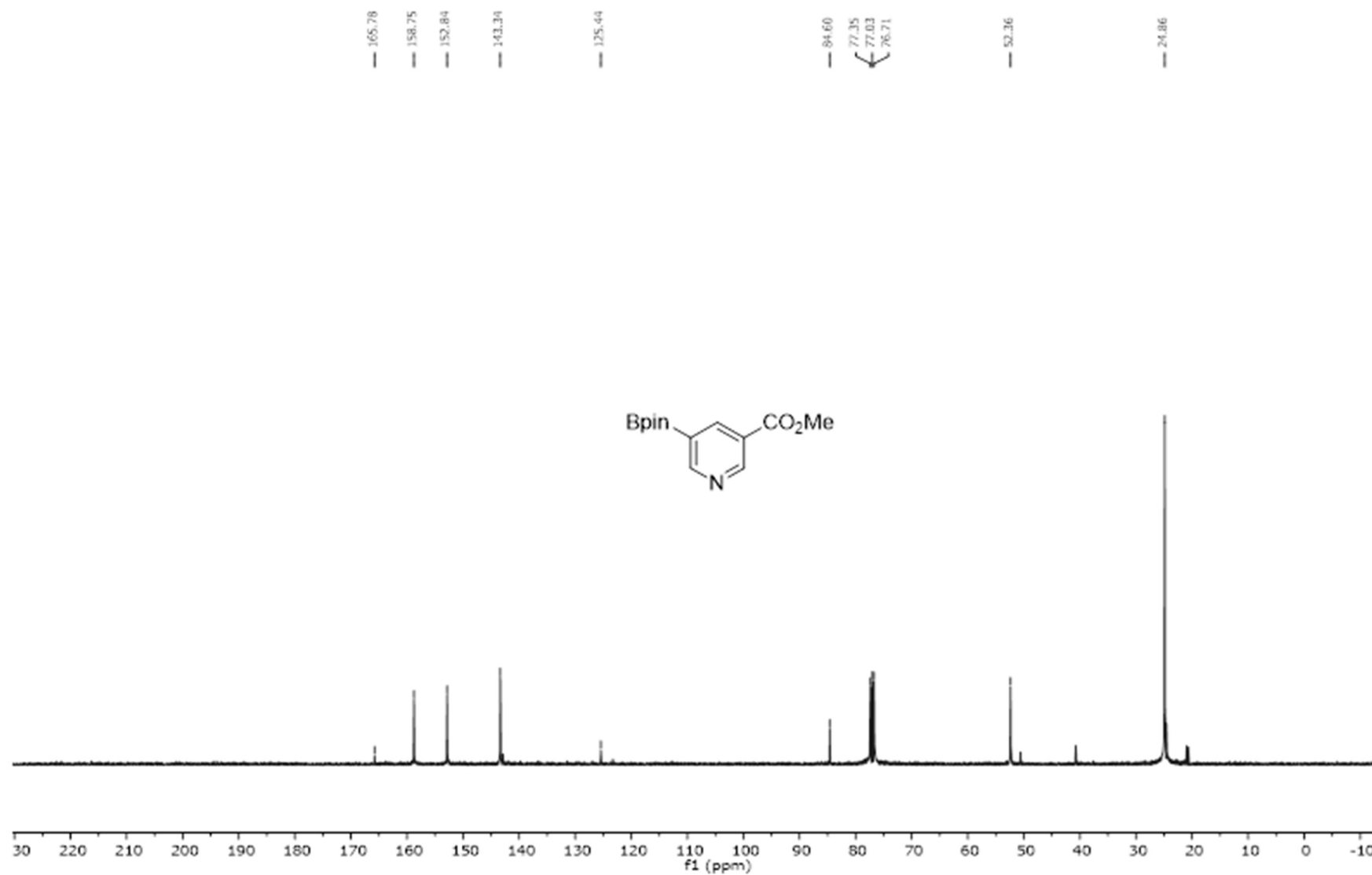
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methoxy-pyridine (**5e**).



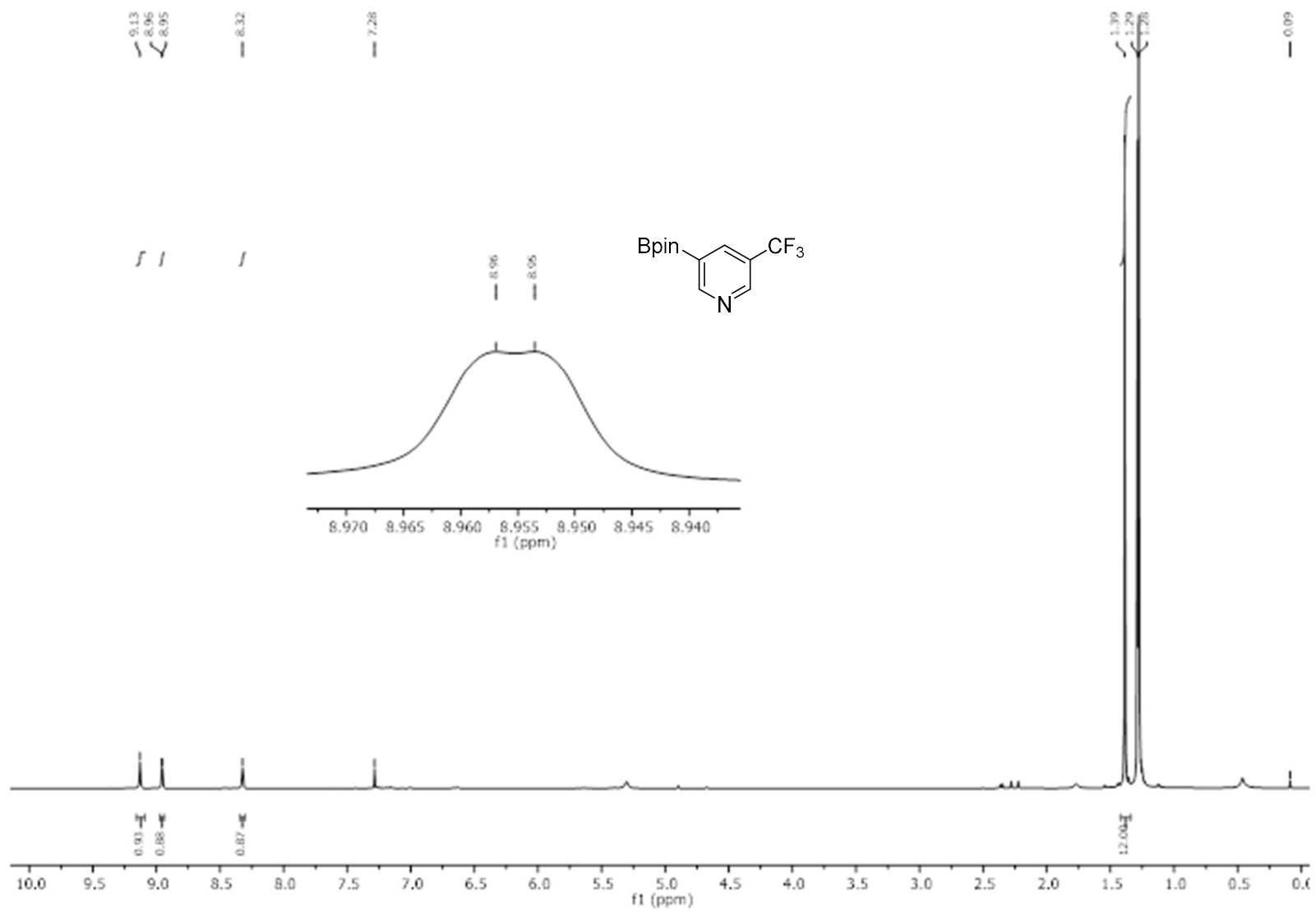
¹H NMR (CDCl₃, 400 MHz) spectrum of 3-pyridinecarboxylic acid, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methyl ester (**5f**).



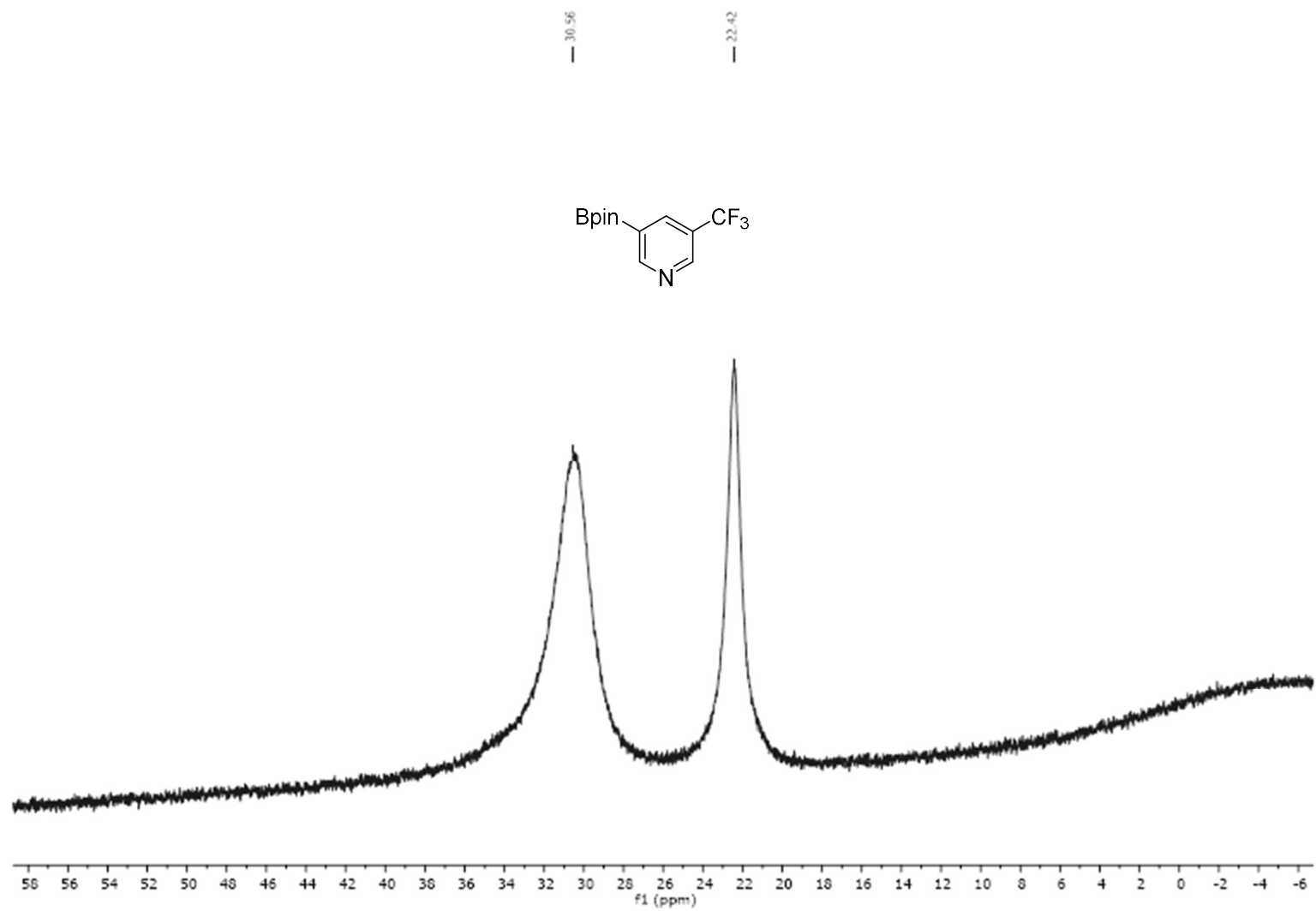
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-pyridinecarboxylic acid, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methyl ester (**5f**).



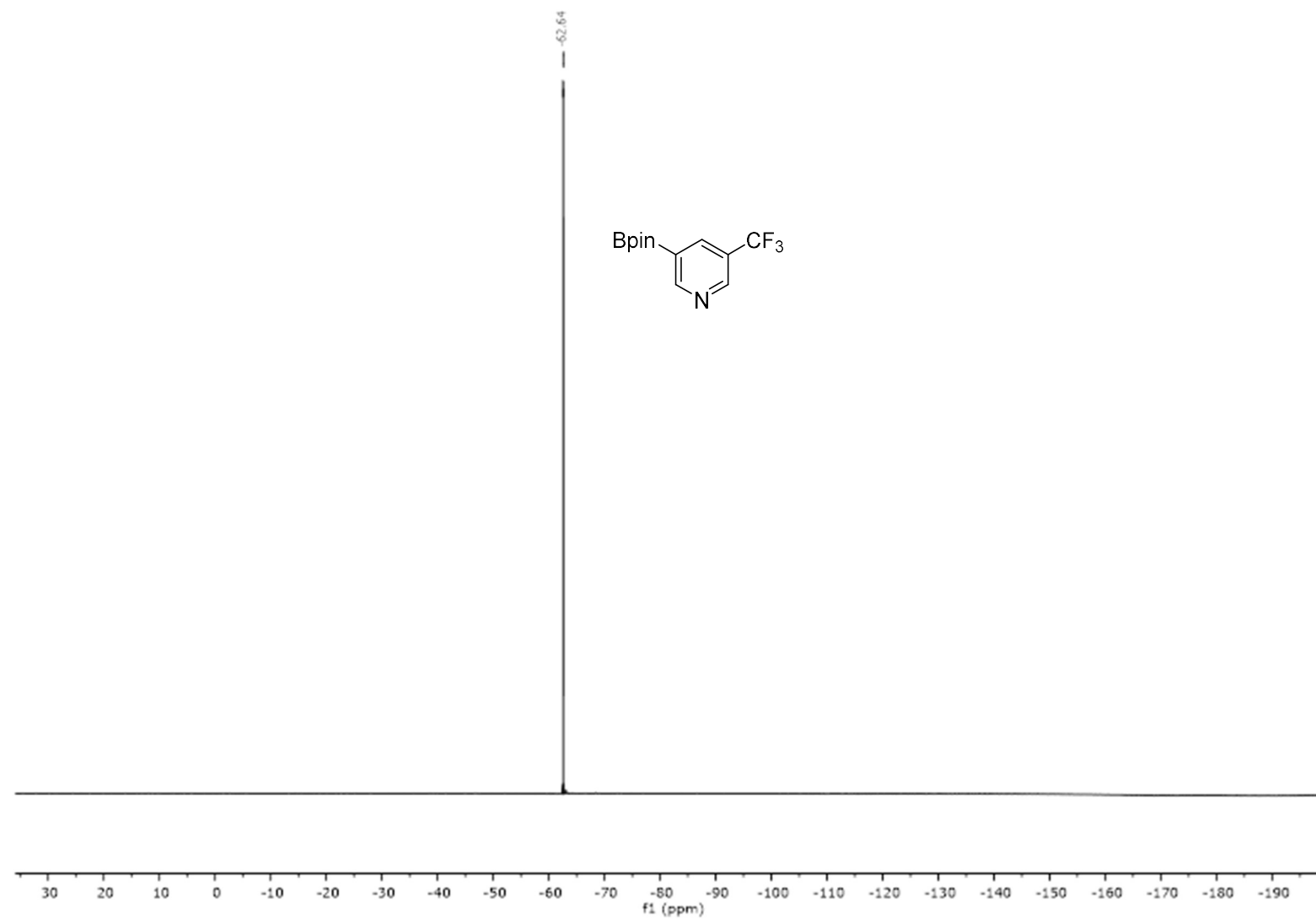
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz) spectrum of 3-pyridinecarboxylic acid, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methyl ester (**5f**).



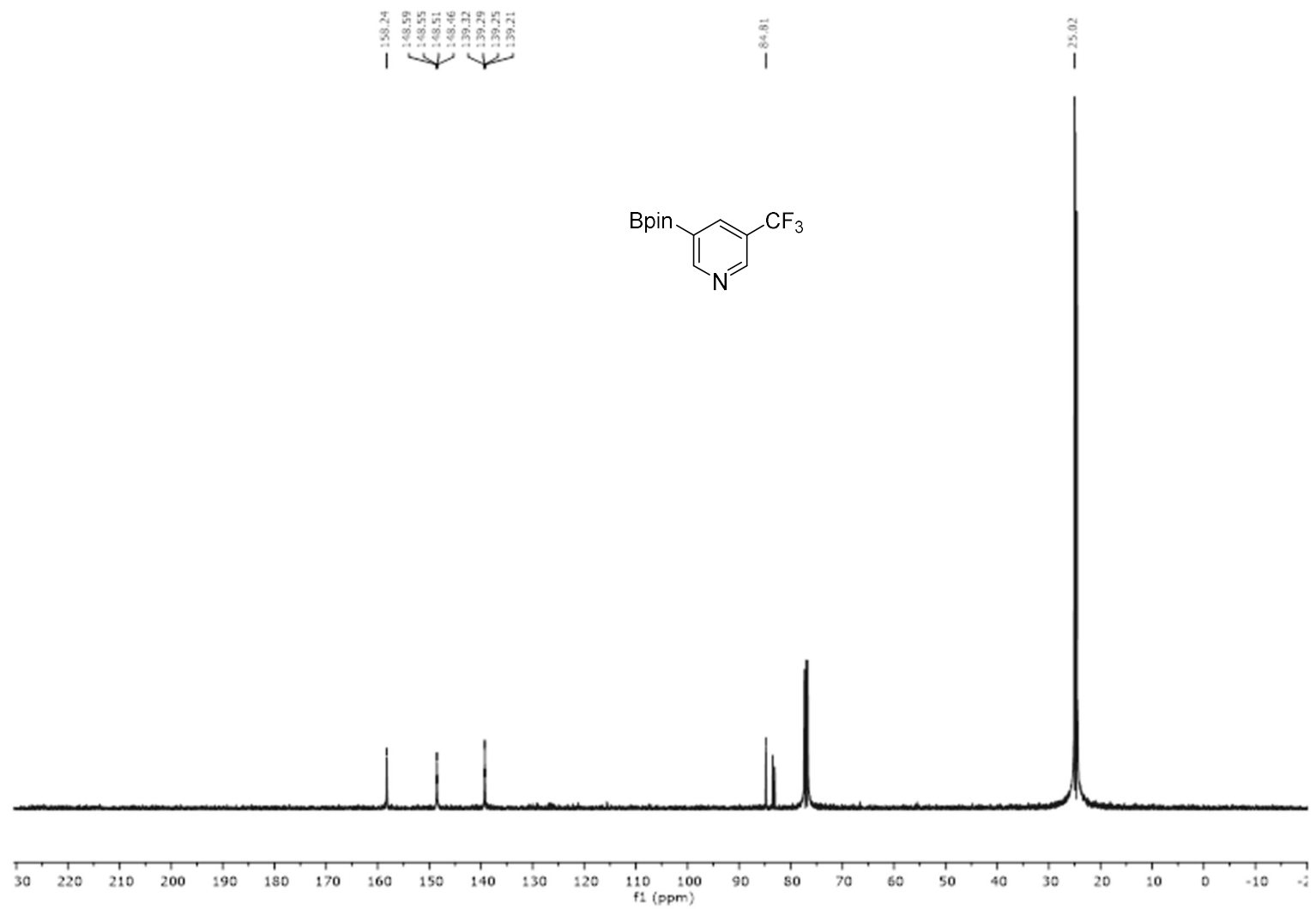
^1H NMR (CDCl_3 , 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylpyridine (**5g**).



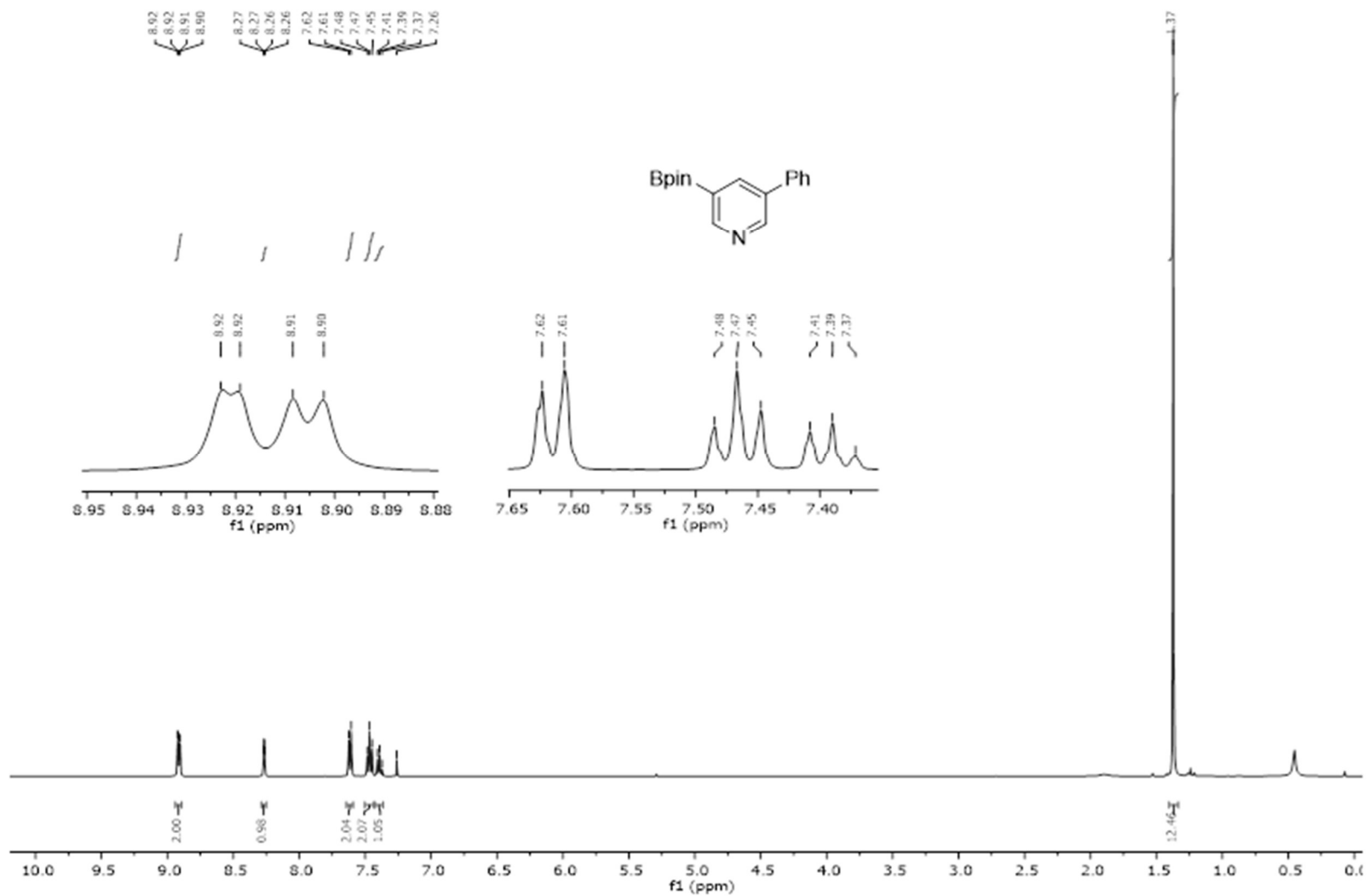
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylpyridine (**5g**).



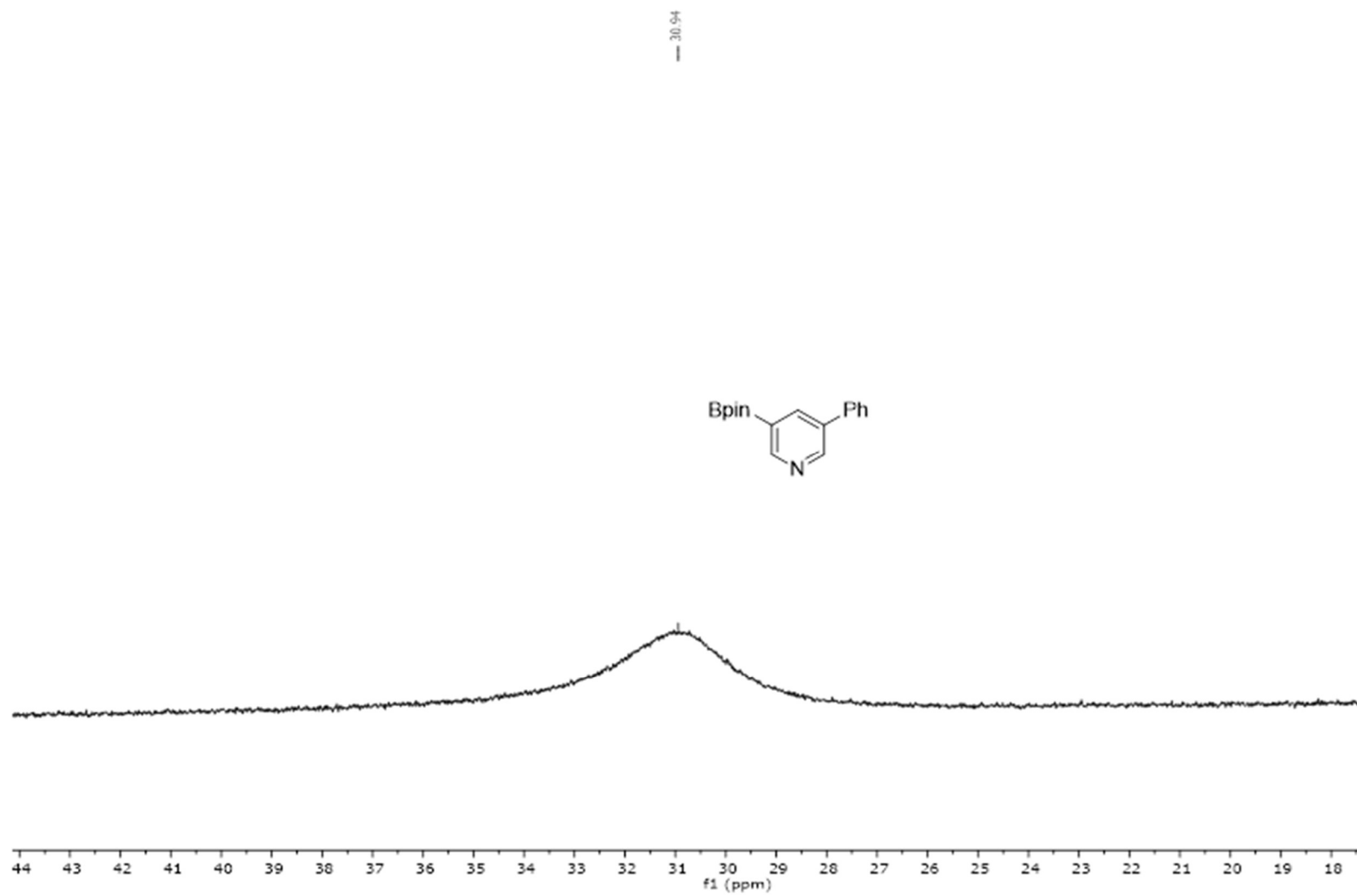
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylpyridine (**5g**).



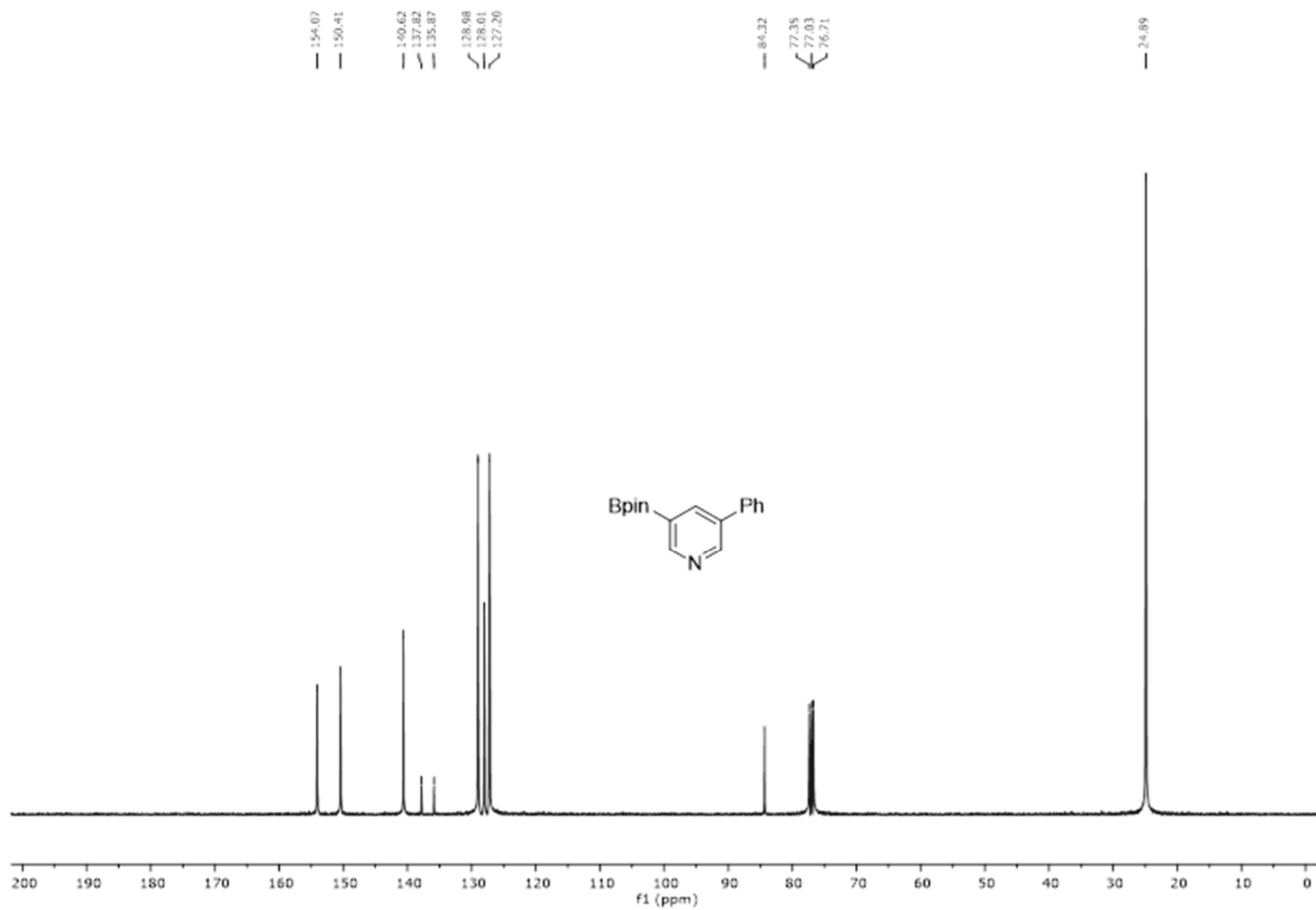
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylpyridine (**5g**).



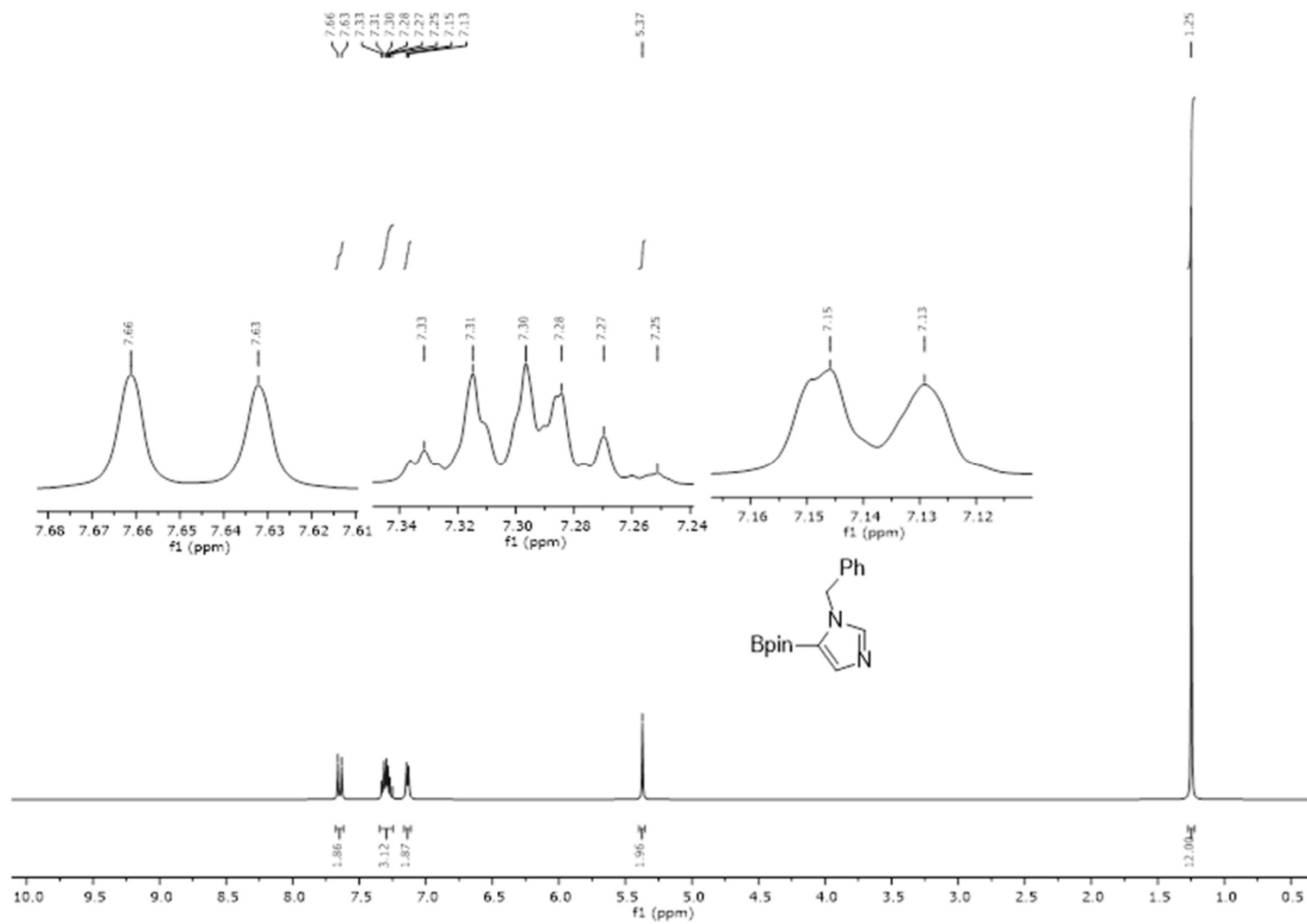
¹H NMR (CDCl₃, 400 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-phenylpyridine (**5h**).



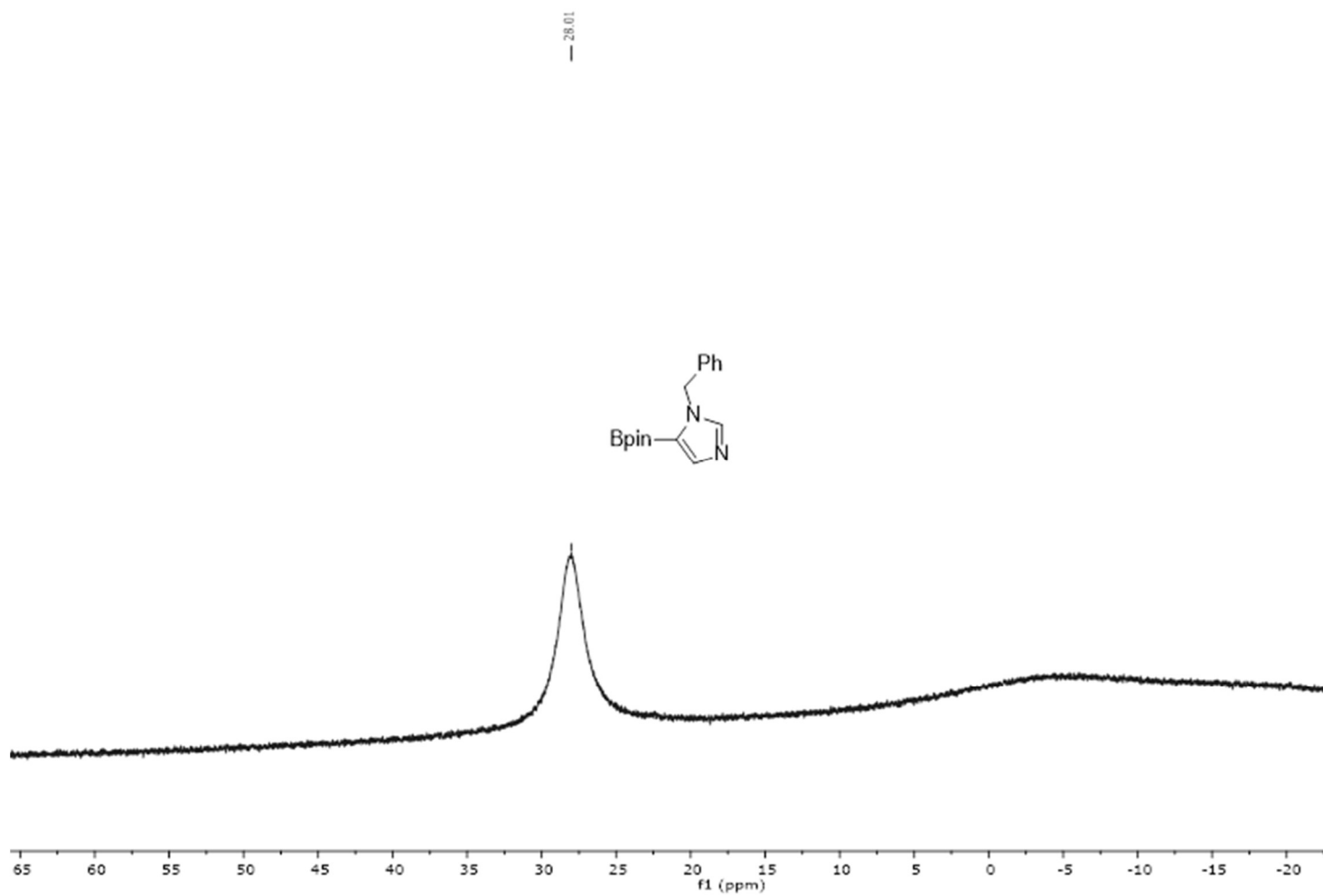
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-phenylpyridine (**5h**).



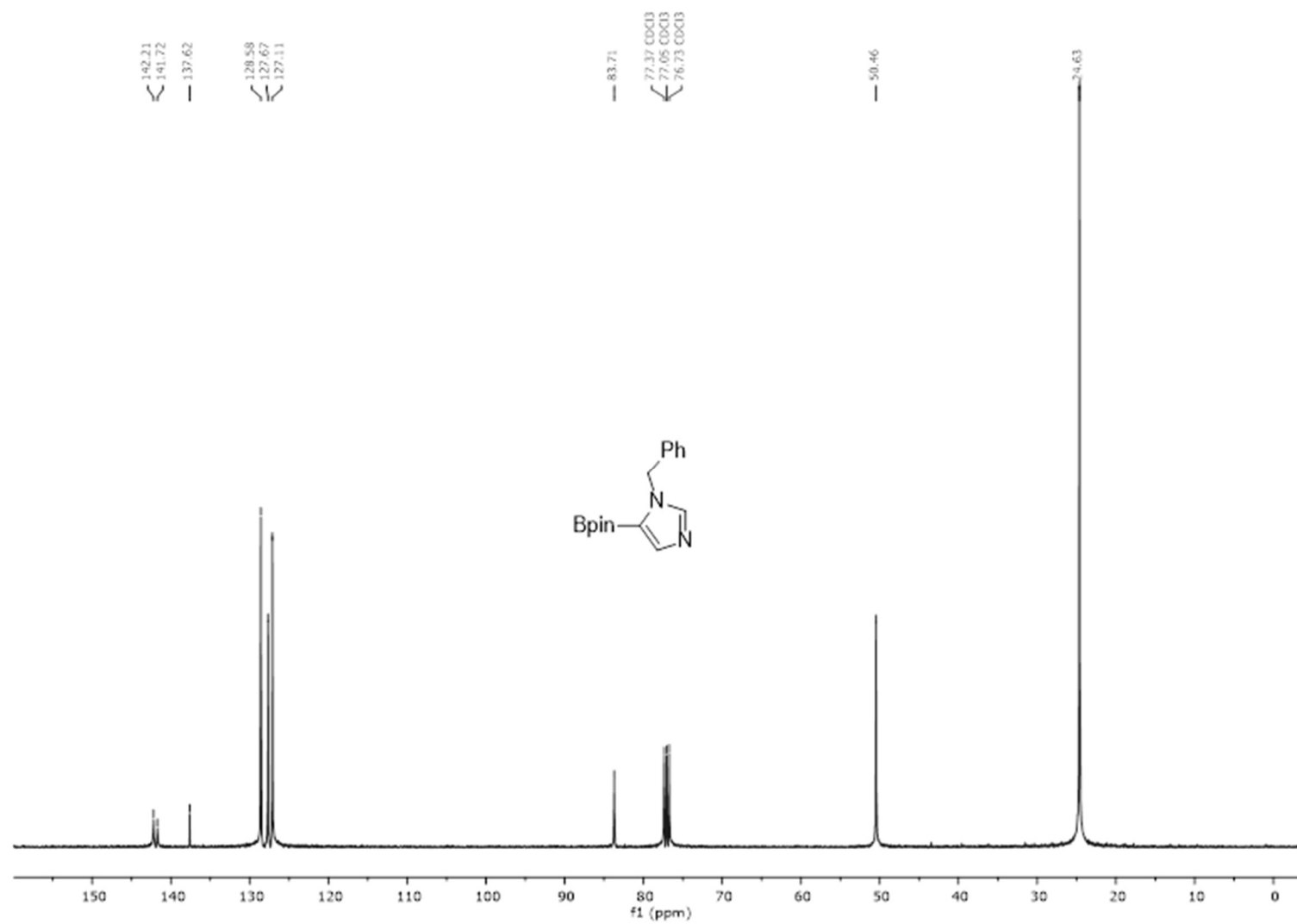
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-phenylpyridine (**5h**).



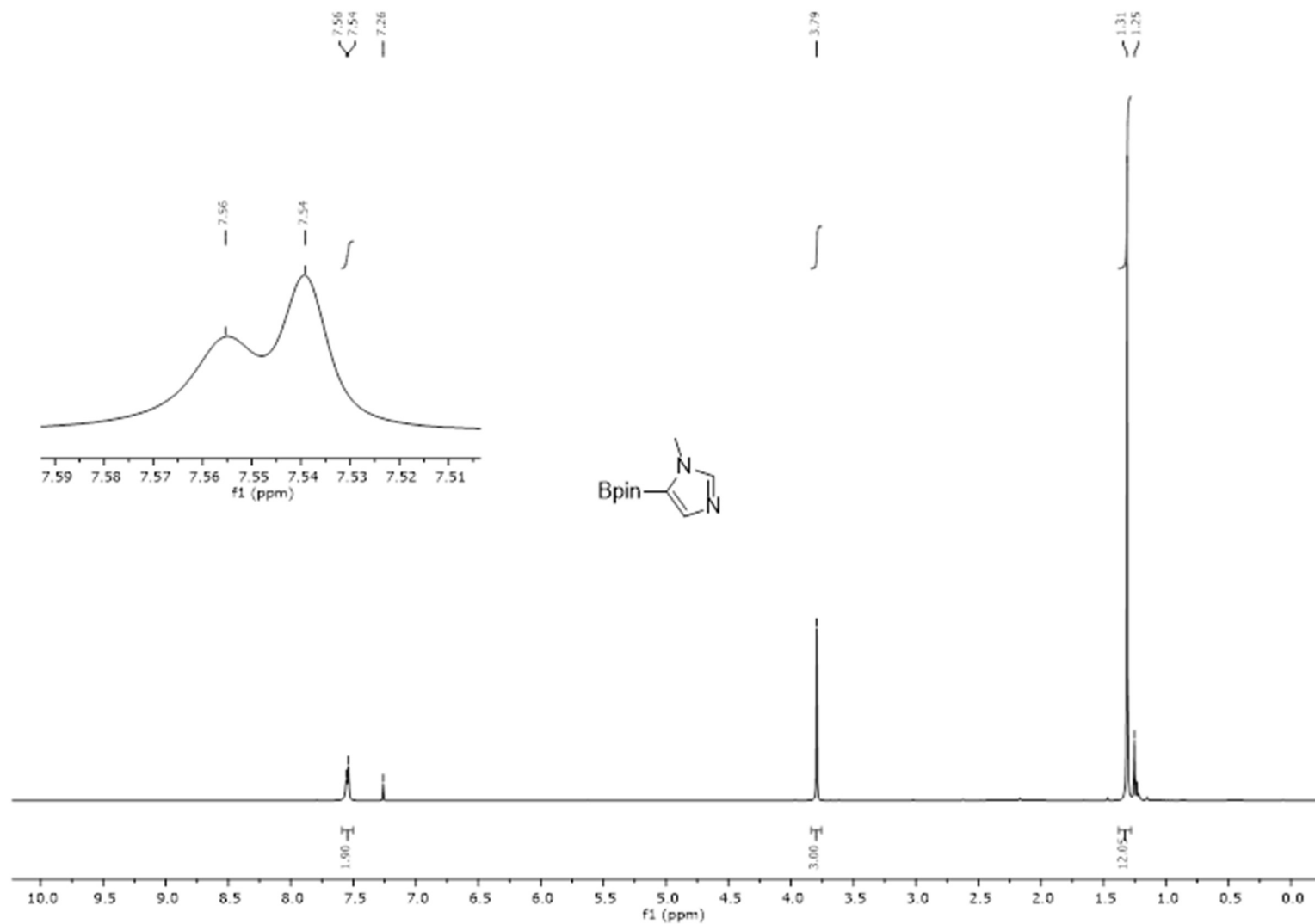
^1H NMR (CDCl_3 , 400 MHz) spectrum of 1-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6a**).



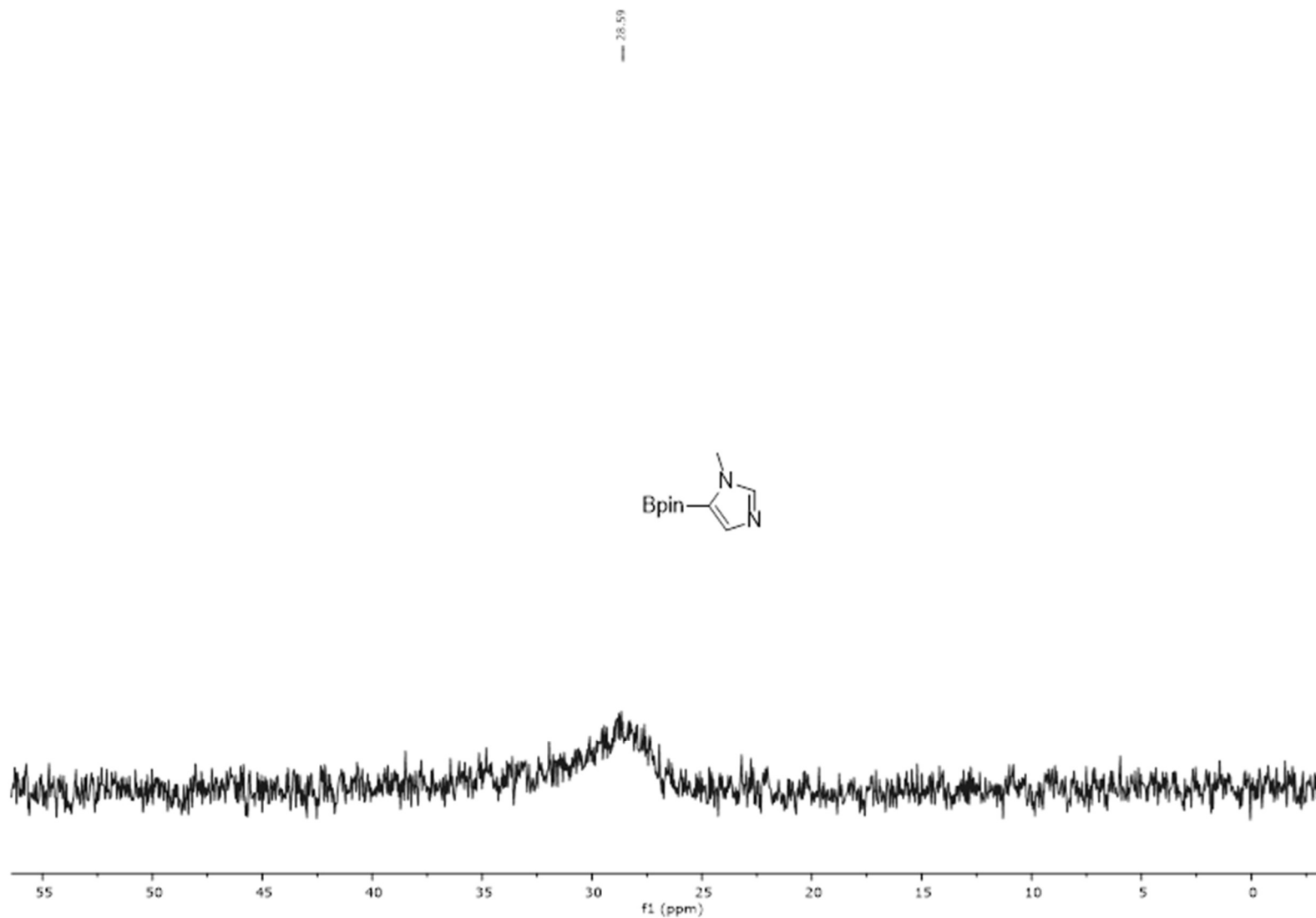
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 1-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6a**).



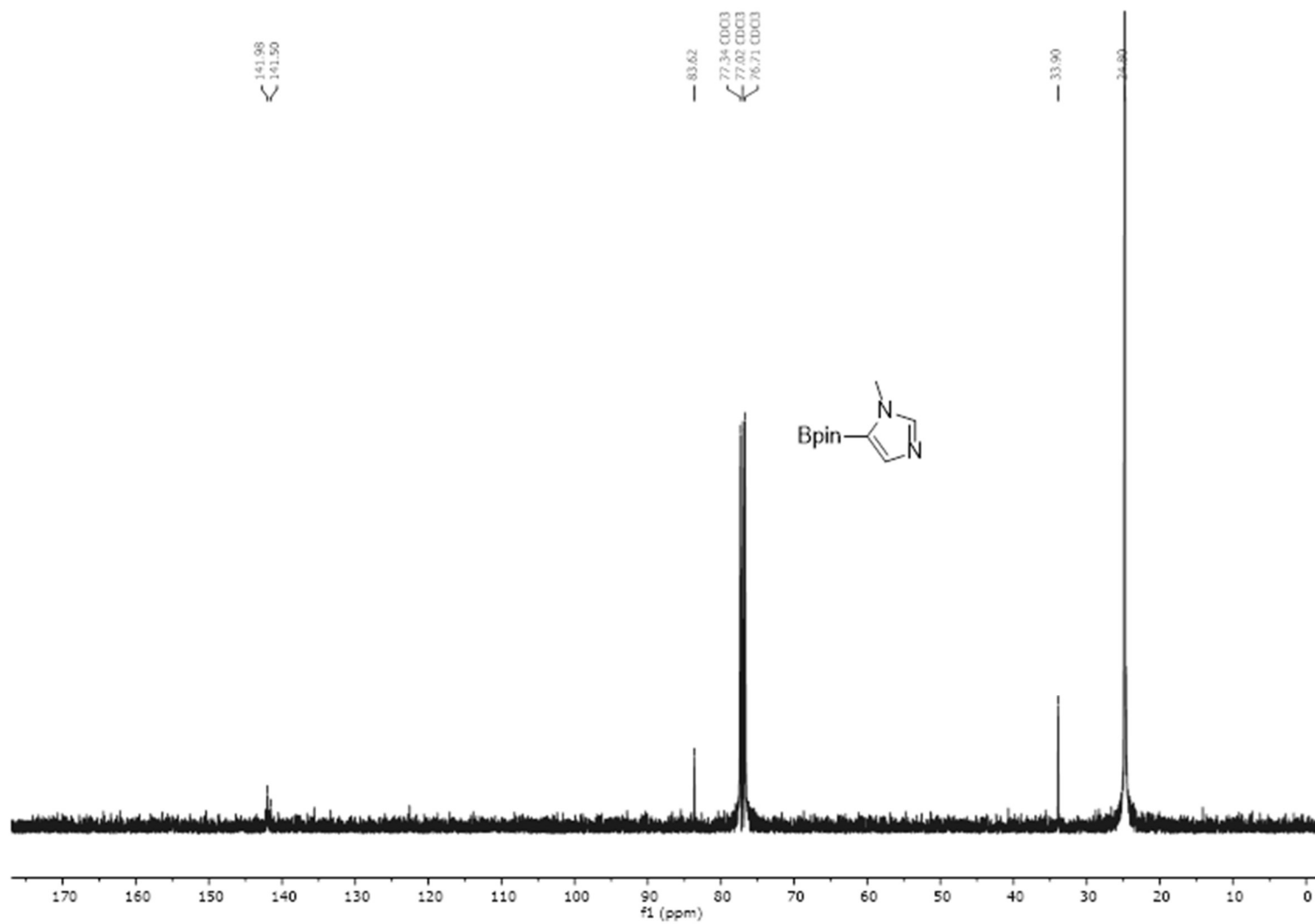
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 1-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6a**).



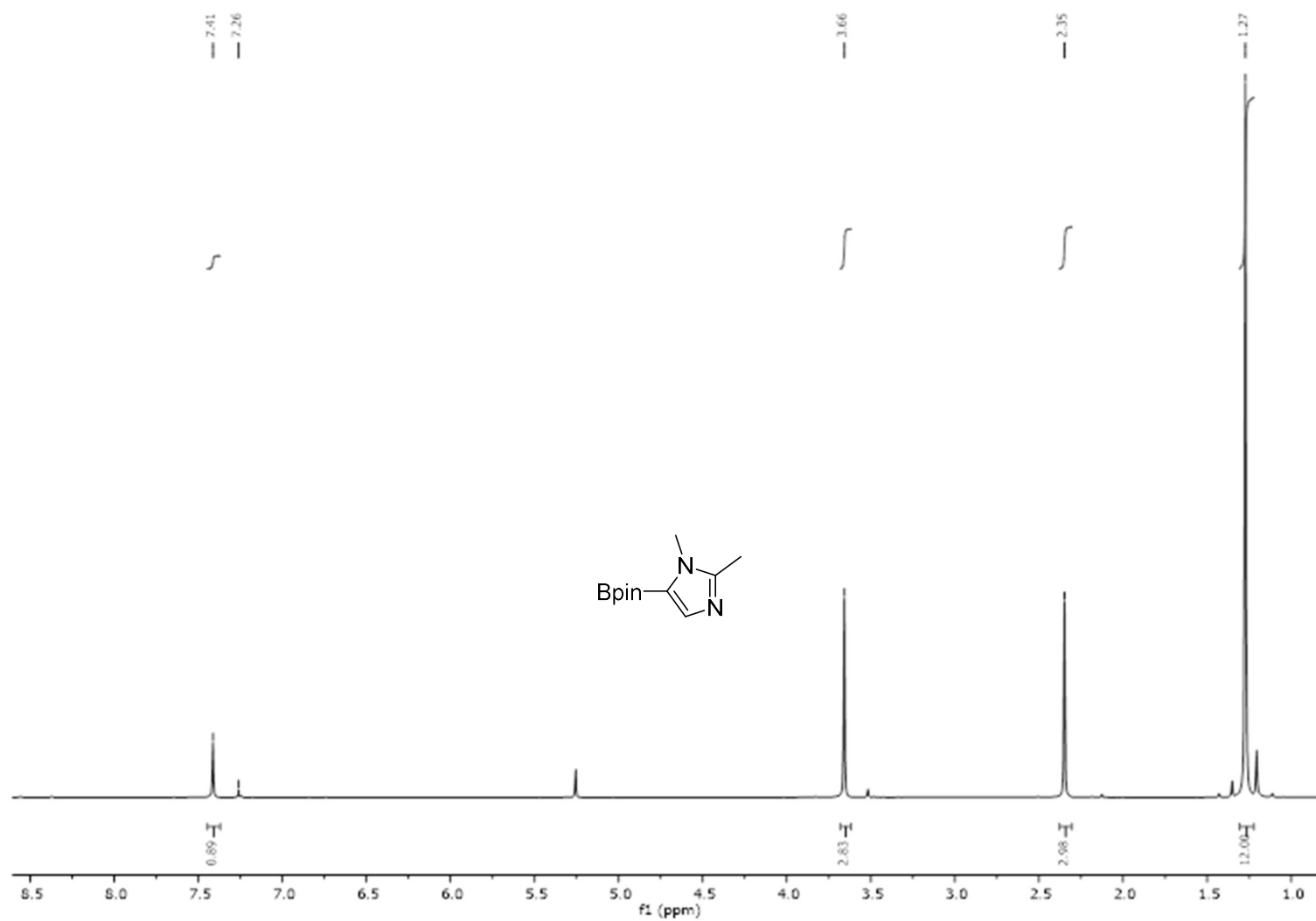
^1H NMR (CDCl_3 , 400 MHz) spectrum of 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6b**).



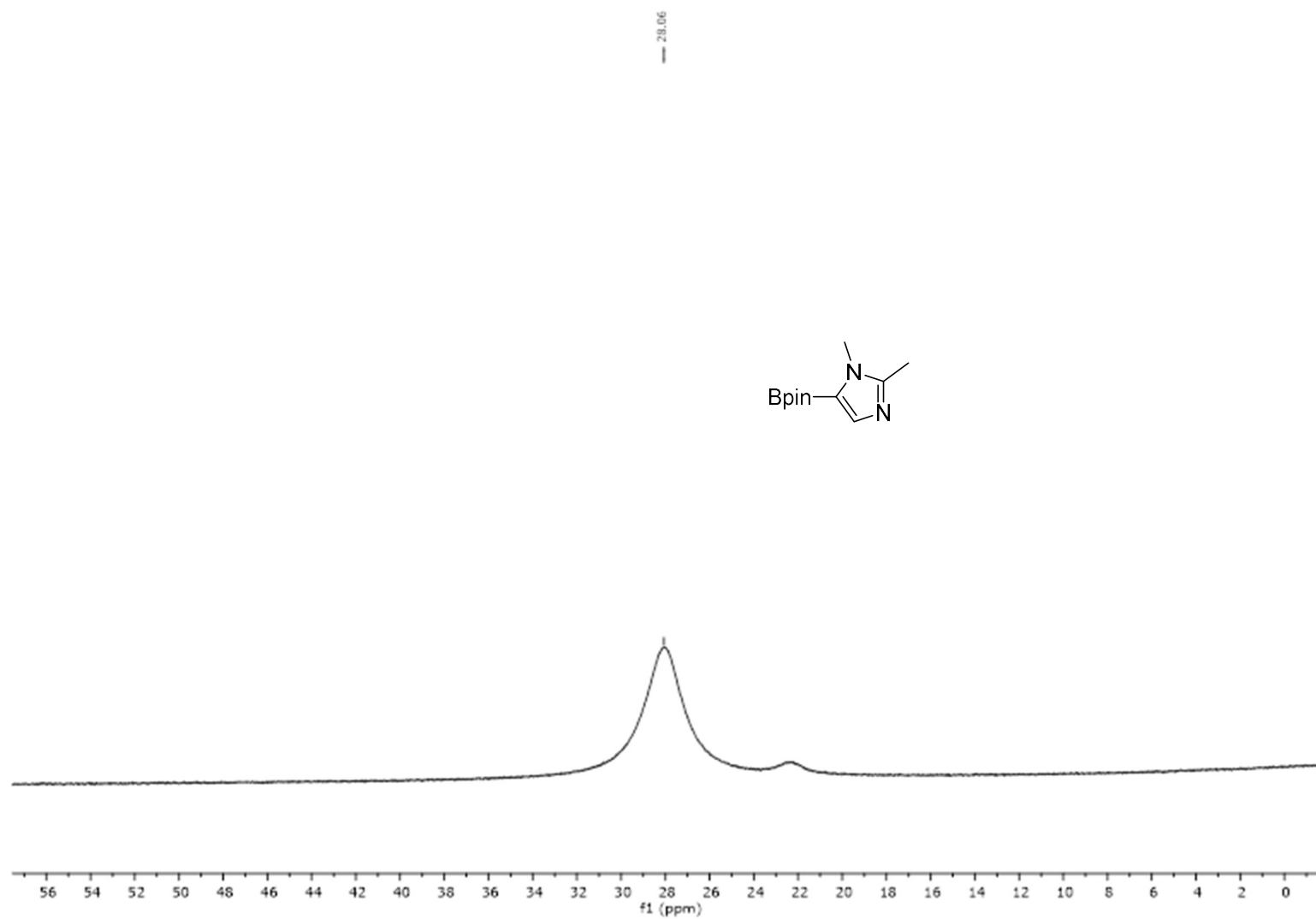
$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6b**).



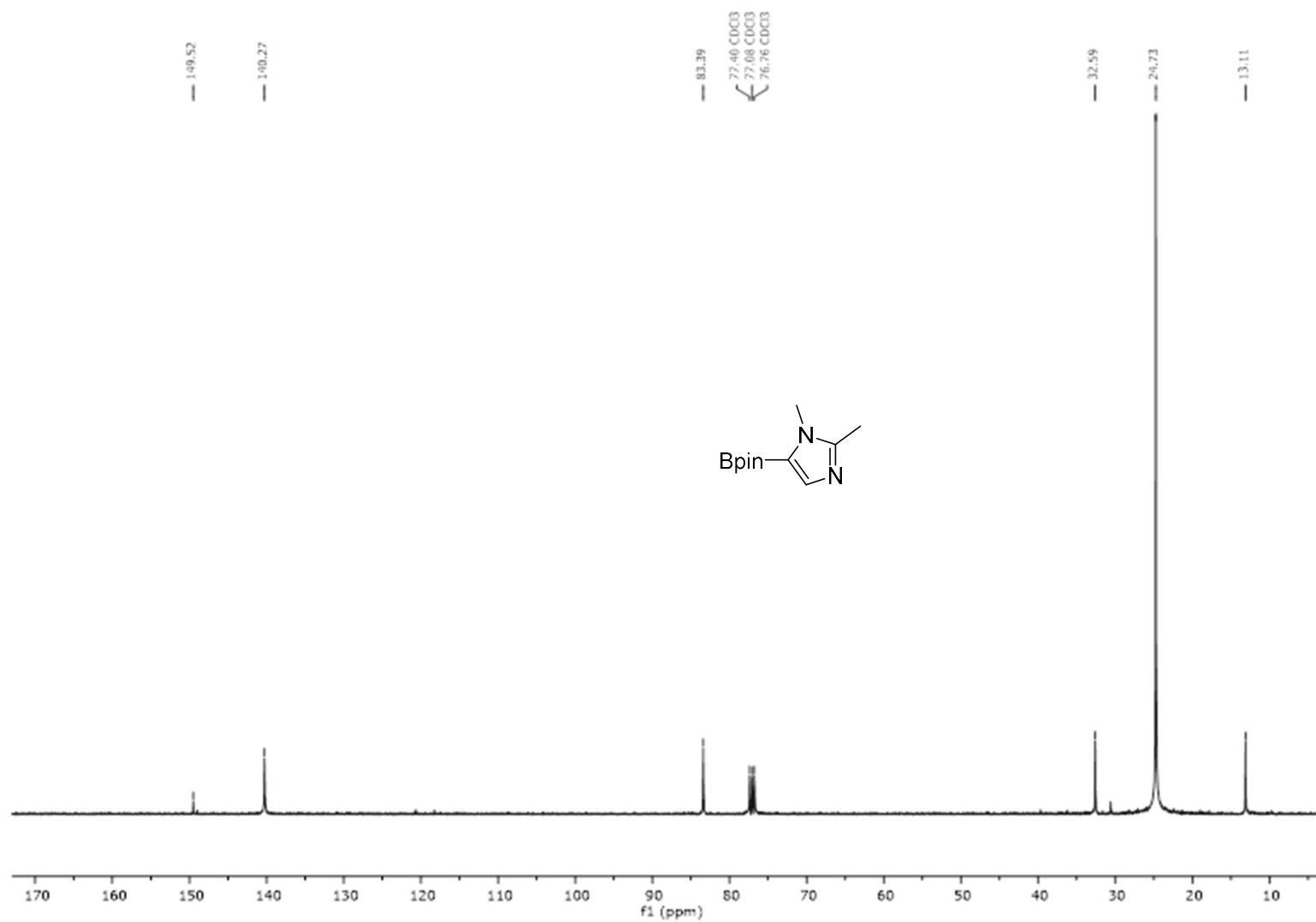
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 101 MHz) spectrum of 1-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6b**).



¹H NMR (CDCl₃, 400 MHz) spectrum of 1,2-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6c**).



$^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) spectrum of 1,2-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6c**).



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) spectrum of 1,2-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-imidazole (**6c**).